

Assessment of Low Cost Novel Sorbents for Coal-Fired Power Plant Mercury Control

Final Report

Reporting Period Start: August 2, 2001

Reporting Period End: March 31, 2004

Prepared by:

Apogee Scientific, Inc.

Report Issue Date: March 2004

DOE Award Number: DE-FC26-01NT41180

Apogee Scientific, Inc.

2895 West Oxford Ave, Suite 1
Englewood, CO 80110-4397
(303) 783-9599

URS Group, Inc.
9400 Amberglen Blvd
Austin, TX 78729

Electric Power Research Institute
3412 Hillview Ave.
Palo Alto, CA 94304-1395

Illinois State Geological Survey
615 East Peabody Drive
Champaign, IL 61820-6964

ADA-ES, LLC
8100 South Park Way, Unit B
Littleton, CO 80120

Disclaimer

“This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.”

Acknowledgements

This project was successful only with the help and guidance by numerous entities. Special thanks to the host facilities and personnel: We Energies' Valley Power Plant and Pleasant Prairie Power Plant and Midwest Generation's Powerton Station. The Electric Power Research Institute (EPRI), Illinois Corn Marketing Board, Illinois State Geological Survey (ISGS), Williams Bio Energy, and the above-mentioned host facilities provided in-kind cost share. Team members on this project include the URS Group, EPRI, ISGS, and ADA-ES. Sorbents evaluated on this project were provided at no cost by numerous vendors.

Abstract

The injection of sorbents upstream of a particulate control device is one of the most promising methods for controlling mercury emissions from coal-fired utility boilers with electrostatic precipitators and fabric filters. Studies carried out at the bench-, pilot-, and full-scale have shown that a wide variety of factors may influence sorbent mercury removal effectiveness. These factors include mercury species, flue gas composition, process conditions, existing pollution control equipment design, and sorbent characteristics.

The objective of the program is to obtain the necessary information to assess the viability of lower cost alternatives to commercially available activated carbon for mercury control in coal-fired utilities. Prior to injection testing, a number of sorbents were tested in a slipstream fixed-bed device both in the laboratory and at two field sites. Based upon the performance of the sorbents in a fixed-bed device and the estimated cost of mercury control using each sorbent, seventeen sorbents were chosen for screening in a slipstream injection system at a site burning a Western bituminous coal/petcoke blend, five were chosen for screening at a site burning a subbituminous Powder River Basin (PRB) coal, and nineteen sorbents were evaluated at a third site burning a PRB coal. Sorbents evaluated during the program were of various materials, including: activated carbons, treated carbons, other non-activated carbons, and non-carbon material.

The economics and performance of the novel sorbents evaluated demonstrate that there are alternatives to the commercial standard. Smaller enterprises may have the opportunity to provide lower price mercury sorbents to power generation customers under the right set of circumstances.

Table of Contents

1.0 Introduction	1
2.0 Executive Summary.....	3
3.0 Experimental.....	5
3.1 Sorbent Development With Respect To Hg Control.....	5
3.2 Evaluation Methodology.....	6
3.3 Plant Descriptions	8
3.3.1 Midwest Generation's Powerton Station.....	8
3.3.2 We Energies' Valley Power Plant.....	8
3.3.3 We Energies' Pleasant Prairie Power Plant.....	9
3.4 Description of Equipment.....	9
3.4.1 Fixed-Bed Adsorption Test Equipment.....	9
3.4.2 Slipstream Injection Equipment.....	10
3.4.3 By-Product Analysis Equipment.....	11
3.5 Sorbent Descriptions and Selection	12
4.0 Results and Discussion	16
4.1 Sorbent Screening Results	16
4.1.1 Powerton Screening Results.....	16
4.1.2 VAPP Screening Results.....	17
4.1.3 P4 Screening Results.....	18
4.2 Parametric and Long-term Evaluation Results	19
4.2.1 Powerton Parametric Results	19
4.2.2 Powerton Long-term Results	20
4.2.3 VAPP Parametric Results	21
4.2.4 VAPP Long-term Results.....	22
4.2.5 P4 Unit 1 Parametric Results	22
4.2.6 P4 Unit 2 Parametric Results	23
4.3 By-product Results	25
4.3.1 Mercury Analyses on By-product Samples.....	25
4.3.2 Landfill Simulation Tests.....	27
4.3.3 Leaching Tests	29
4.3.4 Desorption Tests	31
5.0 Economic Analyses	32
6.0 Conclusions	35
Appendix A. Description of Mercury Monitors and Sampling Procedures	37
A.1 Description of Mercury Monitor.....	37
A.2 Sampling Procedures and QA/QC	38
A.3 Bench Scale Fixed Bed Adsorption Test Device	39
Appendix B. By-Product Equipment and Procedures	41
B.1 Procedures.....	41
B.1.1 Air Stability Testing Procedure and Conditions.....	41
B.1.2 Mercury Desorption Tests.....	44
B.1.3 Leaching Test Procedure and Conditions.....	45

Appendix C. Sorbent Information	46
Appendix D. Laboratory Sorbent Fixed-Bed Evaluations	47
References	49

Figures

Figure 1. PoCT Residence Time Chamber.	10
Figure 2. PoCT configured for TOXECON evaluations.	11
Figure 3. Results from sorbent screening at Powerton. Injection concentration ~ 1.5 lb/Mmacf.	17
Figure 4. Results from sorbent screening at VAPP at an injection concentration ~ 2.0 lb/Mmacf.	18
Figure 5. Results from sorbent screening on P4's Unit 1. Batch injection concentration equivalent to 1 lb/Mmacf for 1 hour.	19
Figure 6. Comparison of mercury removal at 300°F and 350°F at Powerton.....	20
Figure 7. Comparison of mercury removal for sorbents at VAPP at 315°F and 350°F...	22
Figure 8. Mercury sorbent parametric evaluations on Unit 1 at P4.....	23
Figure 9. Parametric sorbent evaluations on P4's Unit 2 with and without SCR on line at a gas temperature of 300°F. Repeated data shown where available for individual sorbents.	24
Figure 10. Parametric sorbent evaluations on P4's Unit 2 with SCR on line at a gas temperature of 300°F.....	24
Figure 11. Parametric sorbent evaluations on P4's Unit 2 with SCR on line at two gas temperatures. Repeated data shown where available for individual sorbents.	25
Figure 12. Sorbent comparison for mercury removal at the three test sites.	35
Figure A-1. Sketch of mercury measurement system.....	37
Figure A-2. Photograph of Apogee mercury S-CEM installed at a field site.....	38
Figure A-3. Bench Scale Fixed Bed Adsorption Test Device.....	40
Figure B- 1. Schematic of the Landfill Simulation Test Set Up.....	41
Figure B-2. Photograph of the Room Temperature Landfill Test Set Up.	43
Figure B-3. Photograph of the 140°F Landfill Test Set Up.....	43

Tables

Table 1. Sorbent Equilibrium Adsorption Capacity Measured in the Laboratory and at Powerton.	13
Table 2. Sorbent Equilibrium Adsorption Capacity Measured in the Laboratory and at VAPP.	13
Table 3. Descriptions of Sorbents Evaluated at Powerton.....	14
Table 4. Descriptions of Sorbents Evaluated at VAPP.....	15
Table 5. Descriptions of Sorbents Evaluated at P4.....	15
Table 6. Powerton By-product Sample Mercury Concentration and LOI Data Summary.	26
Table 7. VAPP By-product Sample Mercury Concentration and LOI Data Summary....	26
Table 8. Results of Powerton Room Temperature Landfill Simulation Tests.....	27
Table 9. Results of Powerton 140°F Landfill Simulation Tests.	28
Table 10. Results of VAPP Room Temperature Landfill Simulation Tests.	28
Table 11. Results of VAPP 140°F Landfill Simulation Tests.	29
Table 12. Leaching Results of the Powerton By-product Samples in SPLP Matrix and Water.....	30
Table 13. Leaching Results of the VAPP By-product Sample in SPLP Matrix, Water, 0.1M Na ₂ CO ₃ , and 0.1N H ₂ SO ₄	30
Table 14. Powerton By-product Samples Desorption Profile.....	31
Table 15. Sorbent Pricing Comparison.....	34
Table B-1. Landfill Simulation Carulite Change Schedule (± 1 week).....	42
Table D-1. Results from Laboratory Fixed-Bed Mercury Adsorption Capacity Tests on Simulated Low Sulfur Eastern Bituminous Flue Gas.	47
Table D-2. Results from Laboratory Fixed-Bed Mercury Adsorption Capacity Tests on Simulated PRB Flue Gas.	48

1.0 Introduction

On December 15, 2003, the United States Environmental Protection Agency (EPA) announced two options for a proposed rule to reduce the current mercury (Hg) emissions from coal-fired power plants in the United States. The first is a two-phase market-based cap-and-trade approach that assumes “co-benefits” reductions of mercury emissions in 2010, and a cap of 15 tons (13.5 metric tons) after 2018, a reduction of 70% from current levels. The second is a maximum achievable control technology (MACT) approach that establishes separate emission limits for mercury for new and existing coal-fired electric utility steam generating units, respectively, with compliance expected by December 2007. EPA estimates that the section 112 MACT proposal will reduce national Hg emissions to approximately 34 tons (30.6 metric tons). EPA will promulgate a final rule by December 2004.

With the proposed rules, the mercury emissions will be reduced by 14 tons (12.5 metric tons) by the end of 2007, or by 33 tons (29.5 metric tons) by 2018 depending on the final ruling option. Details of the proposals are given in the Federal Register. Under these proposed rules, some power plants may not need additional mercury controls beyond baseline (MACT floors for specific coal categories are different. For existing units, emissions limit are 2.0, 5.8, and 9.2 lb/Tbtu (0.96, 2.8, and 4.4 µg/J) for bituminous, sub-bituminous, and lignites, respectively). Others may opt to look at high removals for cap and trade. More stringent rules can still result from individual states, which may opt for greater control levels. At this stage, the determination of cost effective control strategies becomes more complex and requires power plants to assess a number of control options that range from low to high mercury removal effectiveness.

Injection of activated carbon upstream of either an electrostatic precipitator (ESP) or a fabric filter baghouse is the retrofit technology that has the widest potential application for controlling mercury emissions in plants that are not equipped with flue gas desulfurization (FGD-s) scrubbers, which includes 75% of all U.S. plants (1). However, sorbent costs represent a large fraction of the overall costs, especially for units equipped with ESPs. In order to make sorbent injection (for mercury removal) more cost effective, it is necessary to either reduce the amount of sorbent needed or decrease the cost of sorbent production.

This program is funded by the Department of Energy’s National Energy Technology Laboratory (NETL) to obtain the necessary information to assess the viability of lower cost alternatives to commercially available activated carbon for mercury control in coal-fired utilities. Sorbent evaluations were conducted by Apogee Scientific, Inc. (Apogee) from June 2002 to January 2004 at three coal-fired utilities. Injection testing was conducted using the Electric Power Research Institute’s multi-Pollution Control Test (PoCT) system configured either as a COHPAC baghouse, or a residence-time chamber (which simulates the mercury removal in the first field of an ESP). Mercury removal across the slipstream injection device was measured with and without sorbent injection.

The three field sites chosen were: Midwest Generation's Powerton Station (Powerton) burning a PRB subbituminous coal, We Energies' Valley Power Plant (VAPP) burning a blend of Western bituminous coal and petcoke, and We Energies' Pleasant Prairie Power Plant (P4) also burning a PRB coal.

Five novel sorbents were evaluated with the slipstream PoCT system at Powerton, seventeen sorbents at VAPP, and nineteen sorbents at P4. Selection criteria for the Powerton and VAPP studies were based upon the performance of the sorbents in laboratory fixed bed evaluations and the estimated cost of mercury control using each sorbent with projected costs of 25% less than commercially available Norit Americas' Darco FGD™ carbon (FGD), which was the baseline sorbent for this project. The P4 evaluations were added at the end of the program and the sorbents selected for testing were based on projected costs being 25% less than FGD carbon. This report presents data collected during these field evaluations, which will provide information to determine costs and capabilities of these novel sorbents for plants burning similar coals.

2.0 Executive Summary

On December 15th 2003, EPA announced that it would regulate mercury emissions from coal-fired boilers by either using a “cap and trade” approach or a maximum achievable control technology (MACT) standard. Sorbent injection (injection of sorbent upstream of a particulate control system) is one of the more promising options for power plant flue gas mercury control. During most of the testing to-date, a commercially available activated carbon from Norit Americas, Darco FGDTM (FGD), was used as the injected sorbent which to-date has limited the option costs for this control application.

This program was funded by the Department of Energy’s National Energy Technology Laboratory (NETL) to obtain the necessary information to assess the viability of lower cost alternatives to commercially available activated carbon for mercury control in coal-fired utilities. Sorbents that had a projected cost savings of at least 25% compared to the current commercial price of the benchmark sorbent, FGD were chosen for this program. This projected cost includes cost for producing the sorbent, transportation, handling, feeding, balance-of-plant impacts, and waste handling costs. This report is a summary of injection testing conducted at three test sites, Midwest Generation’s Powerton Station (Powerton), We Energies’ Valley Power Plant (VAPP), and We Energies’ Pleasant Prairie Power Plant (P4). The injection tests used the Electric Power Research Institute’s multi-Pollution Control Test (PoCT) system configured as a COHPAC baghouse, or a residence-time chamber (which simulates the mercury removal in the first field of an electrostatic precipitator).

The objective of tests conducted during this program was to compare low cost novel sorbents for mercury removal by assessing the effect of sorbent injection on vapor-phase mercury control at the three test sites. Apogee Scientific, Inc. (Apogee) conducted sorbent evaluations from June 2002 to January 2004 at the three coal-fired utilities. Five novel sorbents were evaluated with the slipstream PoCT system at Powerton, seventeen sorbents at VAPP, and nineteen sorbents at P4. Evaluated sorbents are of various materials, including: activated carbons, treated carbons, other carbons, and non-carbon materials. FGD was tested as the benchmark sorbent at all three sites.

The best performing sorbents were carbon-based as demonstrated at the three field locations. Performance of the carbon-based sorbents varied and the mercury removal could not be correlated to the amount of modification (i.e. activation or treatment) performed on the base sorbent. Specialty carbons, such as iodated activated carbon (IAC), were included in the program since they have demonstrated enhanced performance at certain plant sites. Their performance (lower injection concentrations required in some cases) may offset the higher up front cost (currently ~\$7/lb delivered for IAC), which may provide an economic advantage with specific coals and plant operations. Please note the results for the IAC screening were at injection concentrations much less than that of the other sorbents during screening. For the IAC tests, the injection concentrations were 0.6, 1.7, and 0.5 lb/Mmacf for Powerton, VAPP, and P4, respectively.

Non carbon-based sorbents although not as effective as the carbon-based sorbents tested, may have an economic benefit where by-product resale/utilization is an economic consideration. This program did not attempt to validate claims by the sorbent suppliers as to their impact on fly ash reuse. Performance of the sorbents grouped in the “other” category varied depending on the base material (flyash, zeolite, other). The zeolite-based sorbents performed better than the fly ash-based sorbents during sorbent screening at VAPP and P4. Both the Thief and AMS sorbents removed greater than 60% of the incoming mercury in the TOXECON configuration at P4.

Temperature of the flue gas did not significantly affect sorbent performance in the COHPAC or residence chamber configurations at Powerton. At VAPP, mercury removal increased slightly at the higher temperature (315°F to 350°F) for all three sorbents evaluated in the COHPAC configuration but not in the residence chamber configuration. In addition, sorbent performance increased with increased residence time and injection concentration at both VAPP and Powerton. At P4, the impact of increasing the temperature from 280°F to 350°F decreased the mercury removal performance for all sorbents evaluated. The greatest difference was seen at the lower injection rates. Other plant characteristics may influence sorbent performance and the effect of temperature had on sorbent performance may not be universal to all plants burning similar coals as demonstrated in this program.

Re-injection of sorbent/by-product was evaluated at Powerton using the HOK sorbent and demonstrated 53% mercury removal compared to 83% mercury removal with fresh sorbent. Depending on the plant conditions, costs, and mercury removal required, this concept could be an option for reducing mercury sorbent injection control costs.

Results of the by-product analysis demonstrated that no mercury was released during the air stability or leaching evaluations.

Sorbent economics will be driven by the supply and demand of effective sorbents. If there are viable resources located within close proximity of coal-fired utilities, then lower cost options may be available on a case by case basis. Price of the sorbent will also depend on the required mercury reduction needed by the individual utilities. With the information presented on the control of mercury using sorbents for the two coal types of Western bituminous and PRB evaluated during this project, there are a wide range of sorbents that could be made available to satisfy utilities that require 30% to 70% mercury removal when using a similar particulate control scenerio. Other plant issues also need to be addressed when considering sorbent injection with the impact on the sale of by-products being at the top of the list. The sorbent’s overall economic impact needs to be taken into account when considering the control technology and cost of mercury control. Again, the overall cost of the sorbents evaluated during this program were not independly verified. Although larger companies with more marketing infrastructure, reliability, and negotiating power will supply a large share of the sorbent market, smaller enterprises certainly have the opportunity to provide a lower price to their customers under the right set of circumstances.

3.0 Experimental

3.1 Sorbent Development With Respect To Hg Control

Several factors potentially affect the ability of a sorbent to remove mercury from flue gas. These include the mercury species being removed (oxidized vs. elemental), the flue gas composition, process conditions (e.g., gas temperature), sorbent characteristics, and the presence of other active surfaces (e.g., fly ash or calcium sorbents added to remove acid gases). In coal-fired flue gas, vapor-phase mercury is present both as oxidized mercury and elemental mercury (Hg^0). Oxidized mercury is generally assumed to be present as mercuric chloride (HgCl_2), although mercuric oxides or sulfates may form in the presence of active surfaces. The chemical form of mercury potentially affects sorbent performance. Concentrations of other gas components, such as sulfur oxides, nitrogen oxides, chlorine compounds, and water, also affect mercury adsorption. These variables can affect the application of sorbent injection for mercury control since the flue gas composition can vary widely from one boiler to another.

While the above factors influence mercury adsorption and removal, the most important factors are probably the sorbent type and its associated properties. Research by the Electric Power Research Institute (EPRI) and others have been conducted to identify the various properties that enable a given sorbent to effectively adsorb mercury. Additionally, variations in physical properties such as size, shape, effective surface area, and porosity, also may affect sorbent adsorption performance (1).

Research to date has demonstrated that mercury adsorption decreases as the reaction temperature increases or as the bulk mercury concentration in the flue gas decreases (2). These results are evidence of an underlying physical adsorption mechanism.

Flue gas composition significantly affects mercury adsorption to sorbent surfaces. Higher concentrations of SO_2 or NO_x typically hinder mercury adsorption by activated carbons while increasing the HCl concentration enhances adsorption. The presence of NO_x in the flue gas decreases the individual effects of SO_2 , HCl , and temperature. The observed effects of flue gas composition suggest that the mercury adsorption mechanisms are not entirely physical in nature. Most carbon-based sorbents appear to be affected by flue gas composition in similar ways. However, other material-based sorbents may be affected differently indicating different adsorption mechanisms.

Field and laboratory evaluations with experimental activated carbons have identified the sorbent properties that influence mercury adsorption (1,3,4). These include surface area, pore size distribution, and pore volume distribution. Mercury adsorption by some activated carbons showed a direct correlation to specific surface area, micropore volume, and mesopore volume. However, these correlations only held for carbons derived from high-sulfur coals.

The surface functional groups of a sorbent, especially sulfur species, can strongly affect mercury adsorption. Organic sulfur species enhance mercury adsorption much more than inorganic sulfur species. Doping carbon sorbents with sulfur can enhance capacities for

Hg^0 and HgCl_2 when organic sulfur is not present in the raw sorbent. However, the temperature and process used to impregnate the sorbent determines which sulfur functional groups will form and, therefore, the extent of adsorption enhancement (1).

Further studies have identified various waste biomass materials as good sources for producing activated carbons that are highly effective for mercury adsorption. Waste tires could be another good source (4). Since biomass does not need pretreatment and can be carbonized in one step, the cost for carbon production should be relatively low compared to commercial activated carbon. In addition, local biomass sources can be customized for use at neighboring utilities, hence possibly reducing the transportation and overall costs of mercury control.

Laboratory and pilot-scale tests have indicated fly ashes can also adsorb mercury. In general, fly ash adsorbs substantially less mercury than activated carbon at similar conditions. Also, fly ash is generally unable to achieve total mercury adsorption but, rather, adsorbs only a fraction from the gas. However, when considering the high concentration of ash present in flue gas, it is conceivable that, even with relatively low capacities, the ash may be able to remove substantial amounts of mercury from the gas. Previous tests indicated that mercury removal by fly ashes was affected by flue gas composition in a similar manner as activated carbons. Results also suggest that for a given fly ash, the fly ash mercury capacities correlate with the concentration of unburned carbon in the ash. Recent results also indicate that mercury capacity of a fly ash can be increased by a simple chemical activation (4).

Other novel sorbents produced and tested in EPRI programs include various zeolites (4). Zeolites may have less impact on fly ash use since they are basically silica-alumina based material.

Bench-scale fixed-bed adsorption tests have provided a better understanding of the factors that affect mercury adsorption and provide a relative indication of performance for different sorbents. However, the ability of a given sorbent to remove mercury in full-scale systems cannot be predicted based on the laboratory results alone. To predict mercury removal in full-scale systems, EPRI has developed a mathematical model that couples the results obtained in laboratory tests with mass transfer considerations (5,6). The model incorporates characteristics related to the sorbent (e.g., affinity for mercury, specific surface area, and particle size), mass transfer within a given system, total surface area available for adsorption, and duct residence time. The model has been used to determine conditions under which either mass transfer limitations or sorbent capacities control the extent of mercury removal when injecting sorbents into the duct upstream of an environmental control device such as an ESP or fabric filter baghouse. A detailed description of the model as well as predicted results is provided elsewhere (5,6).

3.2 Evaluation Methodology

For this program, evaluating sorbent injection for mercury control began with a series of laboratory and field tests designed to evaluate mercury removal in flue gas specific to the sites tested. To be considered for laboratory evaluation during this program, the sorbent

manufacturer was required to provide evidence that the cost for removing mercury (per pound of mercury removed) will be at least 25% less than that of FGD. This cost includes not only the cost for producing the carbon but transportation, handling, feeding, and waste handling costs that may differ from FGD. In addition, sufficient quantities of the sorbent would need to be available to supply at least 100,000 tons per year to the utility market by 2010.

Once the sorbent manufacturer determined cost and availability, the mercury performance potential was characterized. In order to evaluate the potential of any mercury sorbent and model its performance, the equilibrium adsorption capacity and characteristics of the sorbent must be known. Scientists at the URS Group conducted fixed-bed adsorption (breakthrough) tests to generate sorbent equilibrium data for each of the candidate novel sorbents considered for evaluations at Powerton and VAPP.

Sorbents were screened by measuring their capacity in the laboratory using simulated low-sulfur eastern bituminous or PRB flue gas prior to field-testing in the actual host flue gas. The purpose of these laboratory tests was to evaluate a number of sorbents at conditions similar to those expected at Powerton (27 sorbents) and VAPP (47 sorbents). The test results were used to determine the most appropriate sorbents for the field evaluations. A control sample, Norit America's FGD™ carbon, was used as the benchmark sorbent for this program.

Following laboratory testing, small-scale fixed-bed screening tests on selected sorbents were performed at Powerton (8 sorbents) and VAPP (17 sorbents) using EPRI's mini sorbent test system. The results of these tests were used to determine which samples to test in a series of small-scale slipstream injection tests using EPRI's PoCT system. The test units and respective methods used are described later in this report. For VAPP, some mercury sorbents were later added to the slipstream screening process without going through the laboratory or field fixed-bed screening because of more recent developments in sorbent technology since the start of the program. Sorbents evaluated at P4 were not evaluated in a fixed-bed arrangement because this site was added to the program at a later time.

During slipstream injection evaluations, two particulate-control configurations were tested to assess mercury removal using sorbent injection upstream of a COHPAC baghouse and upstream of an ESP. A COHPAC module designed for sorbent injection is also called TOXECON. In the TOXECON configuration three sets of tests were conducted at both VAPP and Powerton. Sorbent evaluations were as follows:

1. Sorbent Screening. Each available sorbent was injected for about 20 minutes at Powerton (300°F) and 120 minutes at VAPP (315°F) utilizing a continuous injection.
2. Parametric Evaluations. The two most-promising sorbents from screening and economic criteria considerations were tested at various continuous injection rates and two gas temperatures. Each test condition was held constant for approximately 1.5 hours at Powerton and 4 hours at VAPP.

3. Long-term Evaluations. The two most-promising sorbents were tested continuously for 8-12 hours at Powerton and 48 hours at VAPP. The collected solids from the baghouse hoppers were retained for by-product characterization evaluations.

Sorbent injection screening at P4 was conducted at a single batch injection rate (equivalent to 1 lb/Mmacf for 1 hour) and a gas temperature (300°F) using the PoCT system configured as a COHPAC baghouse. The batch injection rate was equivalent to 1.09 grams of sorbent batch injected into the system at two equal quantities (0.545 grams) four minutes apart. Parametric evaluations also utilized batch injections at various injection rates and two gas temperatures.

In the residence chamber configuration (performed at VAPP and Powerton), two selected novel sorbents and FGD were parametrically tested for 60-90 minutes each, with the variables being gas temperature, injection rate, and residence time (2 and 4 seconds).

3.3 Plant Descriptions

3.3.1 Midwest Generation's Powerton Station

The first field site was Midwest Generation's Powerton Generating Station, Unit 5. Slipstream evaluations with the PoCT system began June 12, 2002 and continued until July 17, 2002. Midwest Generation is a subsidiary of Edison Mission Energy and is part of the Edison International family of companies.

The Powerton Unit 5 and Unit 6 boilers are identical B&W cyclone boilers burning pulverized subbituminous coal from the Powder River Basin. Both boilers (nominally 450 MW each) are used to power one turbine, rated at 893 MW. A Research Cottrell electrostatic precipitator with a weighted wire design controls particulate emissions. The nominal specific collection area of the precipitators are 217 and 424 ft²/kacfm.

Based on 1999 EPA Information Collection Request (ICR) coal data (7), the PRB coal at this site has 20 ppm to 250 ppm chlorine, 0.06 to 0.3 µg/g mercury, and 0.4% sulfur. This site is also located adjacent to the Williams Bio-Energy facility that provided one of the biomass-material sorbents evaluated in this project.

3.3.2 We Energies' Valley Power Plant

The second field site was We Energies' Valley Power Plant, Boiler 3. Evaluations began January 22, 2003 at VAPP and were completed April 15, 2003.

VAPP is a cogeneration facility producing steam for the City of Milwaukee and electricity. The boiler is a Riley Stoker front wall-fired, balanced draft boiler burning a mix of pulverized Western bituminous coal (85%) and petroleum coke (15%). The boiler is rated at 650,000 pounds of steam per hour. Riley Stoker Model CCV Low NOx burners are installed in the boiler. An Environmental Elements pulse-jet fabric filter baghouse is used to control particulate emissions.

Based upon coal data provided to EPA during the ICR effort (7), the mercury level in the coal in 1999 varied from 0.011 to 0.11 µg/g, 50 to 1500 ppm chlorine, and 0.87% sulfur. Data on the petcoke consumed at this facility was not available.

3.3.3 We Energies' Pleasant Prairie Power Plant

Tests were conducted at We Energies' Pleasant Prairie Power Plant (P4), Units 1 and 2. Evaluations began November 3, 2003 at P4 and continued until January 22, 2004.

The boilers are R-Turbo units rated at 605 MW each. Particulate emissions are controlled by an ESP. Unit 1 has been retrofitted for a SCR for NO_x control, but currently the catalyst is not in place. Unit 2 has also been retrofitted for an SCR with the catalyst installed and operational. Based on 1999 ICR (7) coal data, the PRB coal at this site has 14 ppm chlorine and 0.11 µg/g mercury.

3.4 Description of Equipment

3.4.1 Fixed-Bed Adsorption Test Equipment

Determination of the equilibrium adsorption capacity of each candidate sorbent was evaluated by mixing the sorbent with quartz sand and packing the mixture in a Teflon sorbent reaction column. Mixing the sorbent with sand reduced the pressure drop through the column and prevented gas tracking through the column. The bed material was supported by a perforated Teflon disk and packed with quartz wool. The column and upstream tubing were heated and temperature controlled to the specific test temperature for at least 1 hour prior to initiating flow through the column. A further description of the fixed-bed equipment is presented in Appendix A.

During testing, a particulate-free gas sample was provided to the reaction column. An Apogee QGIS™ (QGIS) probe was used during field evaluations to inertially separate and filter the fly ash from the flue gas sample. A sample flow of approximately 1-2 liters/minute was continuously passed through the column. The flue gas flowed downward through the column to minimize the chance of selective flow or channeling through the bed. Mercury measurements were made at the inlet and outlet of the column. The amount of mercury exiting the column was measured on a semi-continuous basis until 100% mercury breakthrough was detected.

Following the fixed-bed sorbent evaluation, mercury adsorption breakthrough curves were generated. The percent breakthrough was determined as a function of time by normalizing the measured mercury concentration at the outlet of the sorbent bed to the inlet mercury concentration. The adsorption capacity of the sorbent (µg Hg adsorbed/g sorbent) at any given time "t" is determined by summing the total mass of mercury adsorbed through time "t" (area above the breakthrough curve) and dividing by the sorbent mass. The equilibrium adsorption capacity is defined by the time when the outlet mercury concentration is first equal to the inlet concentration.

3.4.2 Slipstream Injection Equipment

The PoCT system is comprised of several small modules that can be configured in series or interchanged as required by the test program. The gas extraction assembly uses a temperature controlled probe, flow meter, flow control valve, and several induced draft fans. The extraction probe is a 0.75 to 1.5-inch diameter stainless steel pipe, depending upon the flowrate for the configuration. The length of the probe is determined following a velocity traverse of the duct so that the gas extraction location is at the duct's average gas velocity. After extracting a slipstream of gas from the duct, the gas passes through a QGIS™ filter where a particulate-free sample can be obtained for vapor-phase mercury analysis. The gas then flows through the particulate control module(s), another QGIS filter, through a venturi to measure flow, and an automatic flow control valve. The gas flow is controlled from 10 to 50 acfm depending on the configuration and test parameters.

During residence chamber testing, sorbent is injected into an 8-inch diameter stainless steel tube approximately 60-inches in length. The flow through the tube is maintained at nominally 30-50 acfm. This arrangement minimizes wall-effects caused by the smaller diameter inlet piping and transition zones. A sketch of the residence tube arrangement is shown in Figure 1. Two outlet QGIS filters were installed in the residence tube to allow measurement at two different residence times.

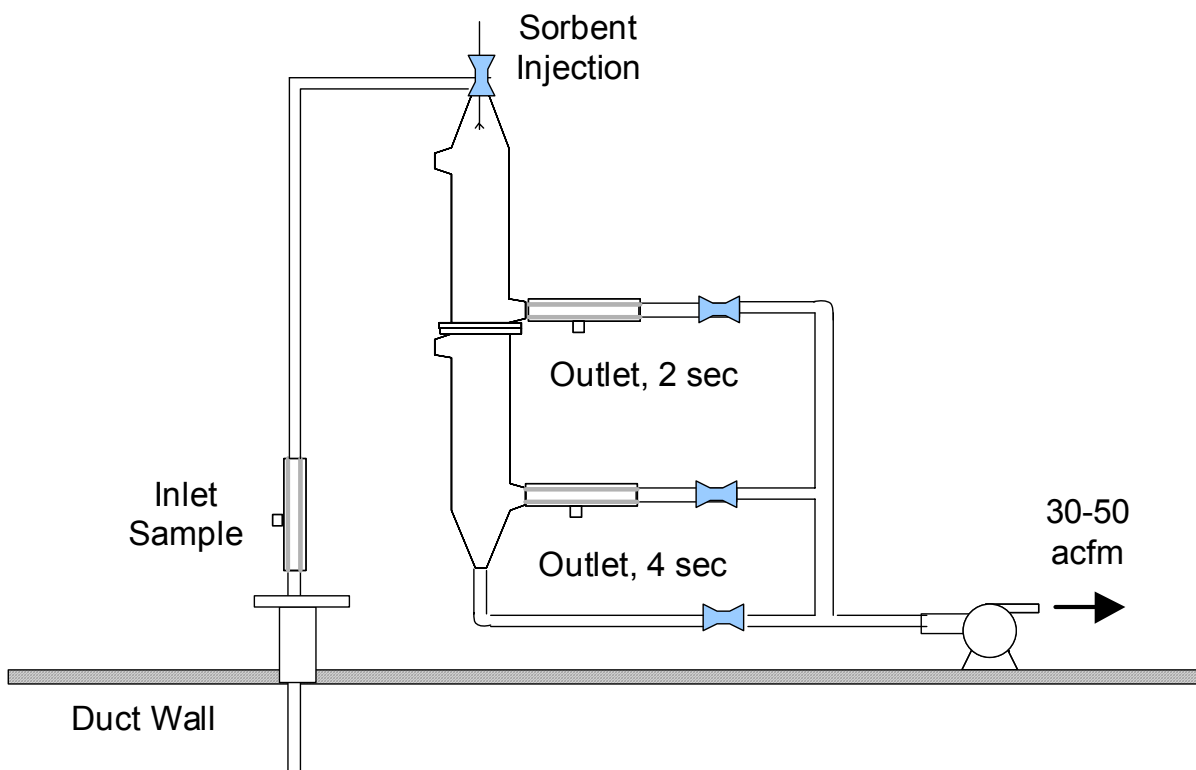


Figure 1. PoCT Residence Time Chamber.

During COHPAC testing, two pulse-jet modules were installed in parallel downstream of a tube-wire ESP to assess the differences in sorbent performance with different bag materials. A COHPAC module designed for sorbent injection is also called TOXECON. Sorbent was injected upstream of the pulse-jet baghouse module and collected on the bag. The filter bags were 24 inches long and had a flat width of 7.562 inches. Bag cleaning was initiated manually during testing and was performed off-line. A sketch of the PoCT TOXECON configuration is shown in Figure 2. As shown, the PoCT pulse-jet module is a top-entry design, which minimizes particulate fall-out into the hopper that often is a concern in small-scale systems.

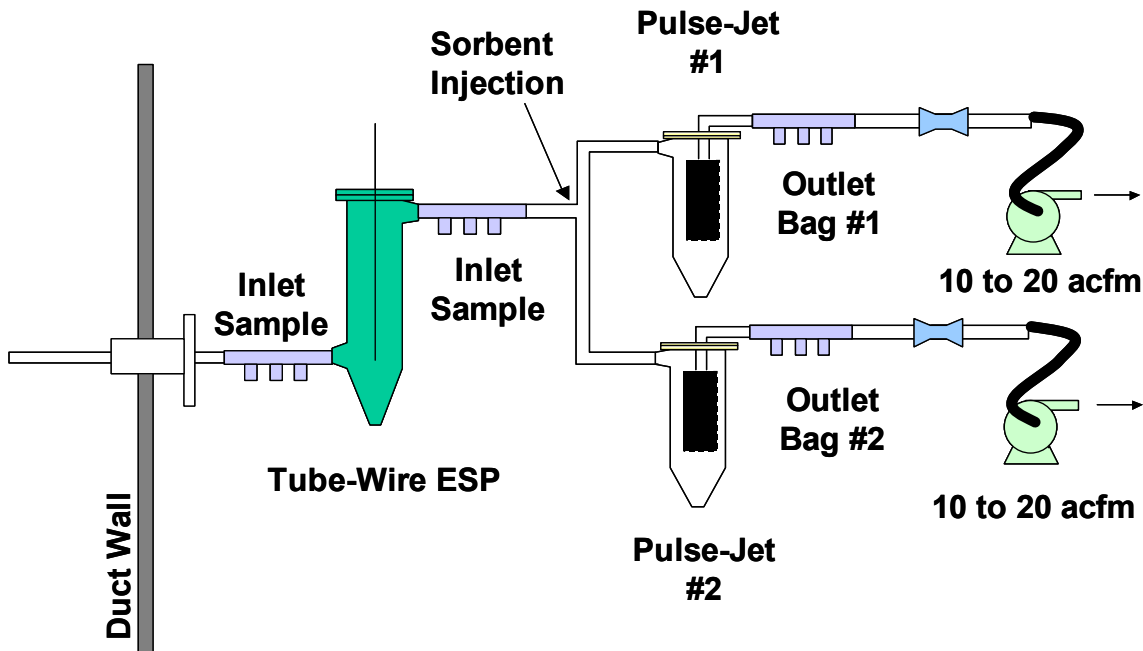


Figure 2. PoCT configured for TOXECON evaluations.

The sorbent injection assembly consists of a small screw feeder and an air eductor. Compressed air is used to carry the sorbent from the eductor to the PoCT injection port. Several custom-designed screw helixes were prepared to provide the low injection rates required for some sorbents during this program.

3.4.3 By-Product Analysis Equipment

During long-term sorbent evaluations at Powerton and VAPP, fly ash and spent sorbent (collectively referred to as by-product) were collected in the baghouse hoppers on the PoCT system. These by-product samples were sent to the URS Group to perform air stability and leaching (using EPA Method 1312- Synthetic Precipitation Leaching Procedure (SPLP)) evaluations. Equipment used during by-product evaluations are described in Appendix B.

3.5 Sorbent Descriptions and Selection

Sorbent properties are the most important parameters controlling the effectiveness of a duct injection process for mercury removal. Under numerous sorbent development programs by EPRI and others, many promising low cost mercury sorbents and processes have been identified. A thorough characterization of over 1,000 sorbents and over 100 fly ashes has been conducted, including evaluating the sorbent chemistry, specific surface area, pore size, particle size, and carbon content of fly ash samples. Additional research has been conducted to determine the effect of treating sorbents such as sulfur impregnation. The proposed sorbents have been tested over two different flue gas conditions. These conditions include simulated flue gas from bituminous coal and subbituminous PRB coal, with both elemental mercury and mercuric chloride. Conditions were chosen to examine the effects of composition and to simulate the flue gases of different coal types. Testing was also conducted at 275°F and 325°F to determine the effect of temperature on sorbent performance.

The most promising novel mercury sorbents developed to date include the following:

- Activated carbon prepared from high organic sulfur coal
- Activated carbon from biomass and waste tires
- Sulfur impregnated sorbents
- Zeolites
- Carbon separated from fly ash (LOI) and unseparated fly ash

Laboratory performance evaluations of forty-seven sorbents were conducted in simulated low sulfur Eastern bituminous flue gas and twenty-seven in a simulated PRB flue gas by the URS Group. A list of sorbent vendors and their sorbents are presented in Appendix C. These sorbents were identified as potential sorbents for testing at VAPP and Powerton based upon economic information provided by the sorbent manufacturers and tested during this program, or by using existing data from URS Group's testing outside this program. A control sample, FGD activated carbon, was also tested as part of the program. Based upon the results of the laboratory fixed-bed screening tests and estimated sorbent costs, eight sorbents were chosen and characterized in the fixed-bed adsorption test device at Powerton and seventeen sorbents for evaluations at VAPP. Of these, five sorbents were chosen as low-cost candidates for injection testing at Powerton and nine sorbents were chosen for VAPP. Eight additional sorbents were added to the screening process after the fixed-bed evaluations were completed at VAPP either by request of the DEO/NETL Program Manager or because suppliers had additional sorbents developed during the project's time frame that meet the original vendor solicitation. Nineteen sorbents were evaluated at P4 with the slipstream PoCT system. The results of the laboratory and field fixed-bed tests for the chosen injection sorbents are presented in Table 1 for Powerton and Table 2 for VAPP. Descriptions of the sorbents are presented in Tables 3 to 5. Different adsorption capacities were measured for the individual

sorbents depending on the location of the evaluations (laboratory or field). This supports the need for field evaluations on sorbents that may be considered for mercury control technology. Results from all laboratory fixed-bed tests are included in Appendix D.

Table 1. Sorbent Equilibrium Adsorption Capacity Measured in the Laboratory and at Powerton.

Sorbent	Test Temp (°F)	Lab, Hg ⁰ Adsorption Capacity µg/g @50mg/Nm ³	Powerton Adsorption Capacity µg/g @50mg/Nm ³
FGD	325	450	264
TDAC	325	227	760
AFR-g	275	314	1,003
	325		
CFA	325	847	259
CS80	275	1,313	328
	325		
HOK300S	275	1,449	670
	325		

Table 2. Sorbent Equilibrium Adsorption Capacity Measured in the Laboratory and at VAPP.

Sorbent	Test Temp (°F)	Lab, Hg ⁰ Adsorption Capacity µg/g @ 50 µg/Nm ³	VAPP Adsorption Capacity µg/g @ 50 µg/Nm ³
FGD	290	618	1,346
	275		
CS80	290	990*	1,094
	275		
CFA	290	1,288	2,004
	275		
TDAC	290	444	568
	275		
HOK	290	1,750*	480
	275		
PSI-C	290	4,047*	55
	275		
LAC	290	555	927
	275		
ARK E-5-CN-02 **	290	115*	16
	275		
STI-20513-B	290		393
Sorbtech L **	290	1,719*	1,194
	275		

* Data for Hg⁰ were not available; measurements are HgCl₂ adsorption capacity µg/g @ 50µg/Nm³

** An alternate sorbent was submitted by supplier that satisfies the requirements

Commercially available FGD carbon, generated from lignite coal, was used during all configurations of PoCT testing at all three sites as the benchmark sorbent. The bulk FOB cost of FGD was \$0.42/lb for this comparison

Another sorbent, IAC, is an iodine-treated sorbent that has demonstrated promising performance during recent EPRI sorbent evaluations. Due to the extra processing steps for the IAC, the cost of this sorbent is over \$7/lb as compared to nominally \$0.42/lb for the FGD. Therefore this sorbent was tested only in screening tests in the TOXECON configuration and was not considered for long-term tests.

Cost estimates for the other experimental sorbents, as provided by the developers, are at least 25% less than the cost of commercially available FGD. The HOK is a commercial product from Germany and the cost quoted by the vendor is approximately 50% the current cost of FGD, not including freight from the nearest Atlantic port for the HOK or Marshall, Texas for the FGD.

The five sorbents tested at Powerton are shown in Table 3. Table 4 and Table 5 are the sorbents that were evaluated at VAPP and P4, respectively. Vendor information on the sorbents is presented in Appendix D. The sorbents are categorized as non-carbon-based (Other), carbon-based, no activation (Carbon), activated carbon-based (AC), and treated carbon-based (TC).

Table 3. Descriptions of Sorbents Evaluated at Powerton.

Sorbent ID	Description	Category
FGD	Texas lignite coal-based commercial carbon, d50 = 18 μm	AC
TDAC	Experimental waste-tire based activated carbon	AC
CFA	Pilot kiln corn-char; experimental, d50 = 15 μm	Carbon
CS80	Experimental carbon from soot, d50 = 6.2 μm	Carbon
HOK	German lignite coal-based commercial carbon, d50 = 19 μm	AC
STI-B	Separated and treated fly ash	Other

Table 4. Descriptions of Sorbents Evaluated at VAPP.

Sorbent ID	Description	Category
FGD	Texas lignite coal-based commercial carbon, d50 = 18 μ m	AC
TDAC	Experimental waste tire-based activated carbon	AC
CFA	Pilot kiln corn-char; experimental, d50 = 15 μ m	Carbon
CS80	Experimental carbon from soot, d50 = 6.2 μ m	Carbon
HOK	German lignite coal-based commercial carbon, d50 = 19 μ m	AC
STI-020513-B, 020930-C, A	Separated and treated fly ash	Other
IAC and IAC 020430-B	Coconut shell-based, iodine impregnated carbon, d50 = 25 μ m	TC
S-1 and E-1-S	Treated fly ash	Other
LAC	Lignite activated carbon	AC
PSI-C	Modified zeolite	Other
A10 and G	Activated carbon with various treatment applications	TC
2002-8680 and 2002-8567	Activated carbon with various treatment applications	TC

Table 5. Descriptions of Sorbents Evaluated at P4.

Sorbent ID	Description	Category
FGD	Texas lignite coal-based commercial carbon, d50 = 18 μ m	AC
A6, A5	Activated carbon base, treated ~ 15 μ m	TC
MC-40, MG-20	Coal based, no added chemicals, 325 mesh	AC
LAC	Lignite activated	AC
CFA	Pilot kiln corn-char; experimental, d50 = 15 μ m	Carbon
CS80	Experimental carbon from soot, d50 = 6.2 μ m	Carbon
IAC	Coconut shell-based, iodine impregnated carbon, d50 = 25 μ m	TC
AMS	Amended silicates (CL-EA-X004)	Other
FA1	Modified unburned carbon, 37-75 μ m	Carbon
CR325A	Low density coal-based	TC
CR325D	Bamboo-based	TC
UMI-FG9B	Bituminous coal based, charred and activated, 200-325 mesh	AC
Sample 1 and 2	Activated carbon, treated, 325 mesh	TC
Thief	Combustion byproduct	Other
HOK	German lignite coal-based commercial carbon, d50 = 19 μ m	AC
PRA58	Zeolite-based, 400 mesh	Other

4.0 Results and Discussion

4.1 Sorbent Screening Results

4.1.1 Powerton Screening Results

Injection screening was conducted at a single injection rate and a gas temperature of 300°F using the PoCT system configured as TOXECON. During the initial screening period, the sorbents were injected at an injection rate of nominally 1.5 lb/Mmacf for 20 minutes to provide a direct comparison of performance. Mercury removal was measured across a Teflon coated woven fiberglass bag. The mercury removal measured during injection of each novel sorbent and FGD is shown in Figure 3. The yellow bars indicate sorbents that are not carbon based, green bars indicate sorbents that are carbon based but no activation, and the blue bars indicate carbon-based sorbents with activation. All carbon-based sorbents demonstrated similar performance, greater than 80% mercury removal, except the TDAC. This material agglomerated prior to feeding. Previous samples of this material did not demonstrate these physical properties. It is possible that the lower mercury removal performance is due to the agglomerating nature of this sample.

Following the initial screening tests, the performance of the two most promising sorbents (CFA and HOK) and FGD were characterized by varying the injection concentration and the operating temperature of the COHPAC baghouse. The most promising sorbents were chosen based upon performance and cost. As mentioned above, the HOK is a commercial product from Germany and the cost quoted by the vendor is approximately 50% the current cost of FGD, not including freight from the nearest Atlantic port for the HOK or Marshall, Texas for the FGD. The CFA was chosen for testing at Powerton because the corn material is available from a corn processing plant near Powerton, thus the shipping costs for the sorbent are expected to be low reducing the overall cost of the product. These factors made these two sorbents the most cost-effective of the group.

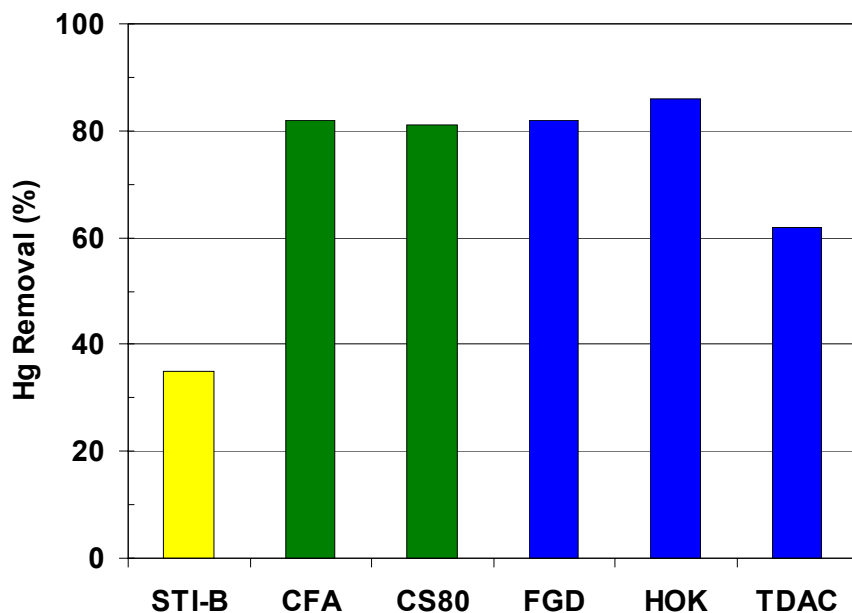


Figure 3. Results from sorbent screening at Powerton. Injection concentration ~ 1.5 lb/Mmacf.

4.1.2 VAPP Screening Results

Sorbent injection screening was conducted at a single injection rate and a gas temperature of 315°F using the PoCT system configured as TOXECON. During the initial screening period, the sorbents were injected at an injection rate of nominally 2.0 lb/Mmacf for 120 minutes to provide a direct comparison of performance. The mercury removal was measured across a Teflon coated woven fiberglass bag. The mercury removal measured during injection of each novel sorbent and FGD is shown in Figure 4. The yellow bars indicate sorbents that are not carbon based, green bars indicate sorbents that are carbon based but no activation, blue bars indicate carbon based sorbents with activation, and red bars indicated carbon based sorbents with additional treatments. Six of the carbon-based sorbents (FGD, CFA, LAC, 2002-8680, 2002-8567, and A10) demonstrated similar performance (mercury removal due to sorbent injection of greater than 90%). Three of the sorbents (HOK, CS80, and G) removed greater than 70% but less than 90% of the mercury in the flue gas. Six of the sorbents (E-1-S, IAC 020430-B, PSI-C, 020513-B, 020930-C, and TDAC) removed less than 50% of the incoming mercury. Two of the sorbents, S1 and A, which were in the “other” category, showed no appreciable mercury removal.

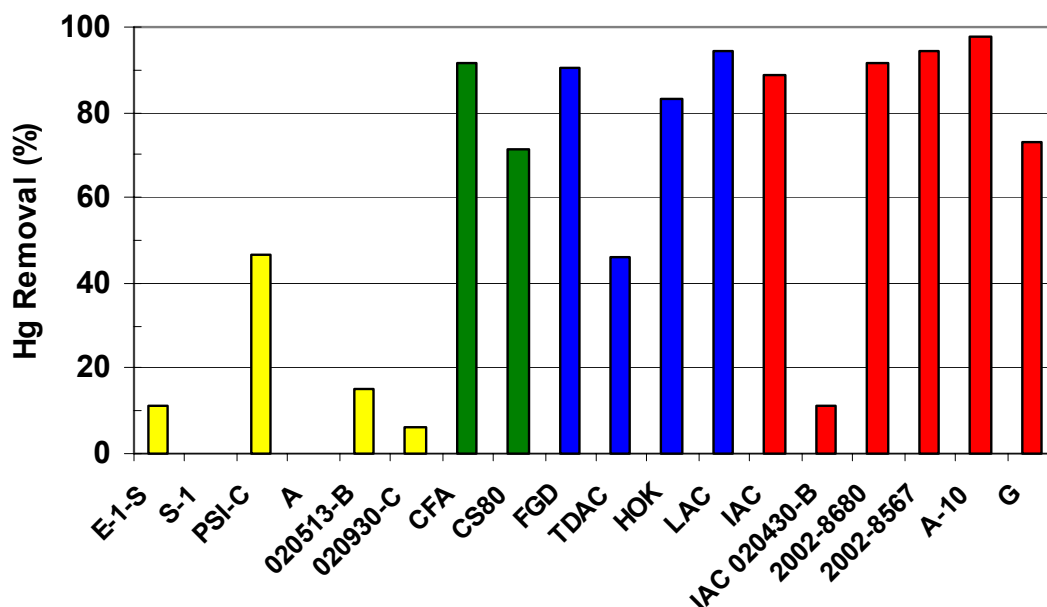


Figure 4. Results from sorbent screening at VAPP at an injection concentration ~ 2.0 lb/Mmacf.

Following the initial screening tests, the performance of the two most promising sorbents (CFA and A10) and FGD were characterized by varying the injection concentration and the operating temperature of the COHPAC baghouse. The most promising sorbents were chosen based upon performance and cost. The CFA was chosen for testing at VAPP because the corn material can be processed nearby, thus the shipping costs for the sorbent are expected to be low reducing the overall cost of the product. Sorbent A10 demonstrated excellent mercury removal and meets the supplier solicitation requirements. These factors made these two sorbents the most cost-effective of the group.

4.1.3 P4 Screening Results

At P4, injection screening on nineteen sorbents was conducted at a single batch injection rate (equivalent to 1 lb/Mmacf for 1 hour) and a gas temperature of 300°F using the PoCT configured as a COHPAC baghouse. The batch injection rate used during screening was equivalent to 1.09 grams of sorbent batch injected into the system at two equal quantities (0.545 grams) approximately four minutes apart.

Mercury removal was measured across a Teflon coated woven fiberglass bag. The mercury removal measured during injection of each sorbent is shown in Figure 5. Again, the yellow bars indicate sorbents that are not carbon based, green bars indicate sorbents that are carbon based but no activation, blue bars indicate carbon-based sorbents with activation, and red bars indicated carbon-based sorbents with additional treatments. Carbon-based sorbents, in general, performed better than those sorbents in the “other”

category. The IAC (not shown in Figure 5) was evaluated at 0.5 lb/Mmacf with a result of 70% mercury removal.

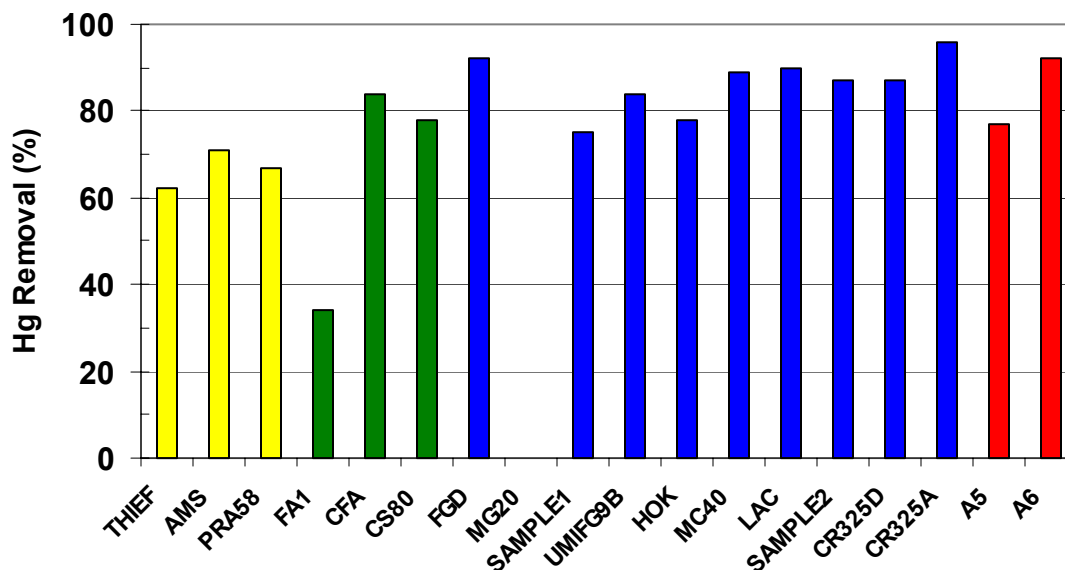


Figure 5. Results from sorbent screening on P4's Unit 1. Batch injection concentration equivalent to 1 lb/Mmacf for 1 hour.

Following the initial screening evaluations on Unit 1, the performance of the three selected sorbents (AMS, A6, and CR325D) and FGD were characterized by varying the batch injection concentration and the operating temperature of the COHPAC baghouse. The selected sorbents were chosen based upon screening performance, novel idea, and sorbent cost. CR325D was chosen over CR325A because the base-material was biomass (bamboo) and was different from biomass sorbents previously evaluated. Cost estimates for the experimental sorbents, as provided by the developers, are at least 25% less than the cost of commercially available FGD. Both the A6 and AMS were chosen for testing at P4 because the sorbents, according to the suppliers, would not affect fly ash sales.

4.2 Parametric and Long-term Evaluation Results

4.2.1 Powerton Parametric Results

During parametric testing, the mercury removal across the baghouse was measured at three sorbent injection rates and two gas temperatures. HOK, CFA and FGD were each tested.

Sorbent performance with respect to gas temperature and injection concentration is presented in Figure 6. As shown, the impact of increasing the temperature from 300°F to 350°F is insignificant, except possibly for the CFA at the lowest injection rate, where some degradation was seen.

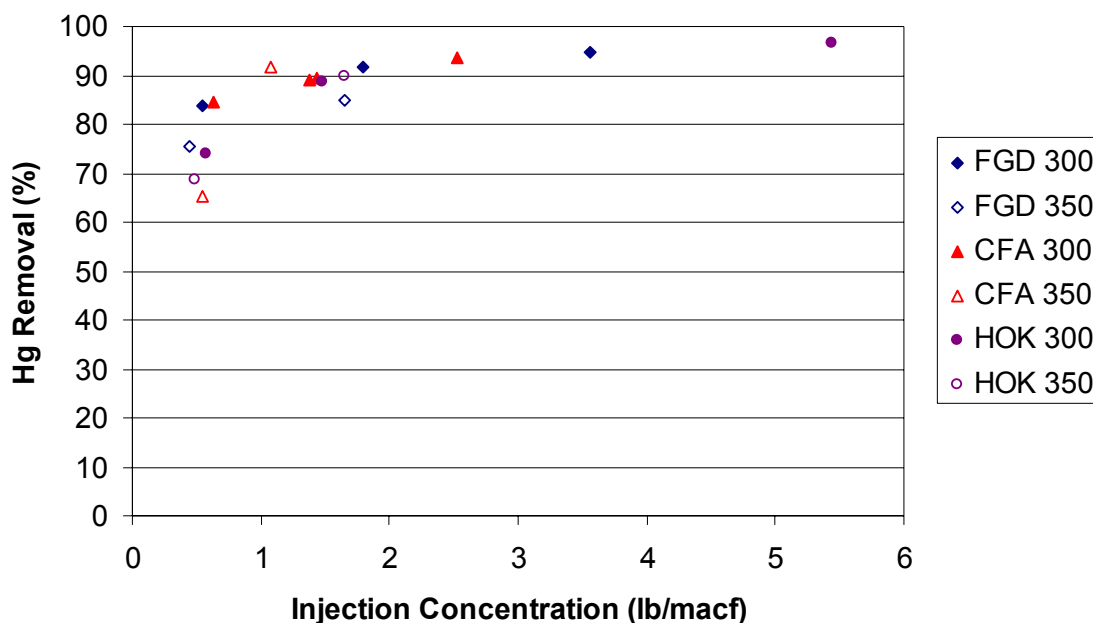


Figure 6. Comparison of mercury removal at 300°F and 350°F at Powerton.

An iodine-impregnated activated carbon (IAC) was also evaluated to determine if injection of a treated carbon would result in higher mercury removal. The IAC was screened at a lower injection concentration than the other sorbents. An injection concentration of 0.6 lb/Mmacf resulted in 72% mercury removal during the screening test, as compared to 82% removal for FGD at an injection concentration of 1.5 lb/Mmacf. To better compare mercury removal performance, the screening results for the IAC and FGD were reviewed alongside the parametric results from the FGD tests. During the parametric tests, the mercury removal at 1.5 lb/Mmacf was 93% (as compared to 82% during the short screening test). At an FGD injection concentration of 0.6 lb/Mmacf, the mercury removal was still relatively high at 84%. This data suggests that the IAC did not demonstrate better mercury removal performance than the FGD in the TOXECON configuration at Powerton.

4.2.2 Powerton Long-term Results

Following parametric testing, a continuous injection evaluation was conducted for CFA, HOK, and FGD in the TOXECON configuration. Two different bag fabrics were installed in the baghouse compartments of the PoCT, one was a Teflon coated fiberglass and the other was a 7.0 denier PPS felt Torcon. The longer-term injection test was conducted for 8 to 12 hours at a targeted injection rate of 2 lb/Mmacf and a temperature of 300°F. Inlet mercury levels ranged from 5 to 7.5 $\mu\text{g}/\text{Nm}^3$. The mercury removal across the bag increased for approximately 2 hours before leveling off to around 90% for

all sorbents. A sample of the material collected in the baghouse hopper during the extended HOK injection test was re-injected to determine the potential of recycling sorbents in a TOXECON configuration. At the screening injection concentration, the recycled HOK/fly ash demonstrated 53% mercury removal as compared to 83% mercury removal with fresh HOK sorbent. The product collected in the hopper during the extended test was nominally 50% sorbent.

By-products collected in each baghouse hopper were sent to the URS Group for by-product evaluations. Results are presented later in the report.

4.2.3 VAPP Parametric Results

Mercury removal across the baghouse during the parametric evaluations of CFA, A10, and FGD was measured at three sorbent injection rates and two gas temperatures. The sorbents were injected upstream of the baghouse modules in the TOXECON configuration.

Sorbent performance with respect to gas temperature and injection concentration is presented in Figure 7. As shown, the impact of increasing the temperature from 315°F to 350°F slightly increased the mercury removal, except possibly for the FGD at the lowest injection rate, where some degradation was seen.

The baseline mercury removal across the TOXECON assembly was not consistent. The natural mercury removal ranged from 5% to 60% depending on the time of the evaluations. LOI has been shown to influence mercury removal in other research. In an earlier study performed by Apogee for EPRI, fly ash analysis was performed and the LOI was measured to be at 35% for both daytime and nighttime operations. EPRI also looked at the variation in steam flow and found that it only varied by 15% for a two-day sample period. However, the loading was nearly twice as high during the evening as during the day, and the size distribution of the night sample was somewhat smaller than the sample collected during the day. Soot blowing did occur occasionally at VAPP and the data collected during those periods was excluded in the analysis. The percent mercury removal presented in this report is percent removal due to sorbent injection.

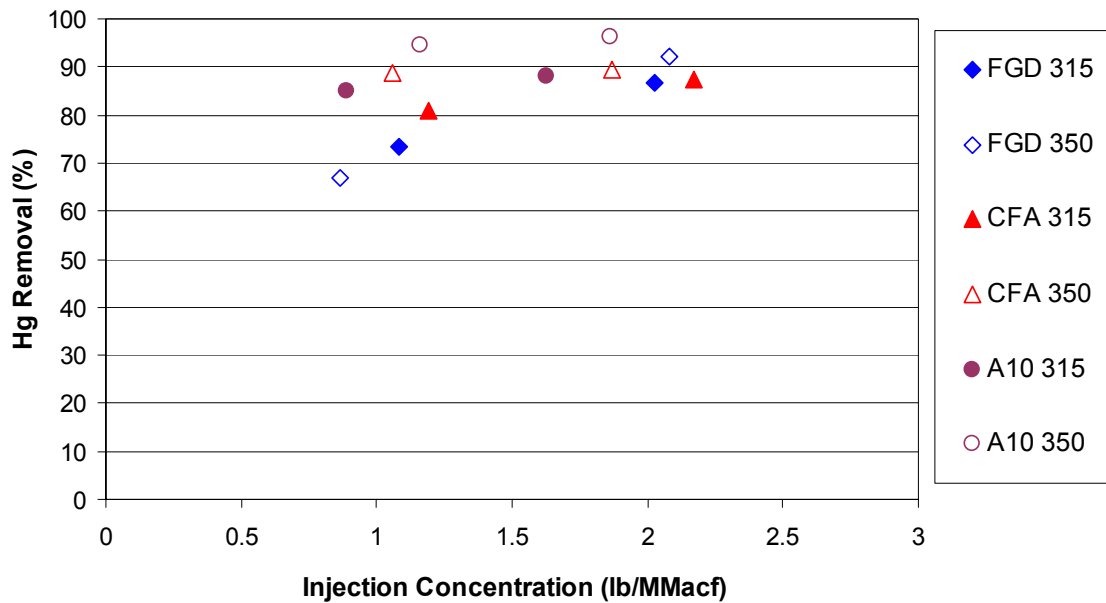


Figure 7. Comparison of mercury removal for sorbents at VAPP at 315°F and 350°F.

4.2.4 VAPP Long-term Results

Following parametric testing, a long-term continuous injection evaluation was conducted for the two sorbents (CFA and A10) and FGD in the COHPAC configuration. Two different bag fabrics were installed in the baghouse compartments of the PoCT, one was a 2.7 denier PPS (Ryton) felt and the other was a 7.0 denier PPS felt Torcon. The Torcon bag is a high permeability fabric designed to retain more dust cake and operate at a lower pressure drop than a standard 2.7-denier Ryton felt bag. The longer-term injection tests were conducted for 48 hours at a targeted injection rate of 2 lb/MMacf and a temperature of 315°F. The mercury removal across the baghouse increased for approximately 2 to 12 hours before leveling off. Both the CFA and A10 reached the percent mercury removal observed in the parametric evaluations within 1 hour of injection. The FGD reached similar results but only after 12 hours of injection. The percent mercury removal for all sorbents ranged from 94% to 99%.

By-products collected in each baghouse hopper were sent to the URS Group for by-product evaluations. Results are presented later in the report.

4.2.5 P4 Unit 1 Parametric Results

Following the screening evaluations on Unit 1, the performance of the three novel sorbents (AMS, A6, and CR325D) and FGD were characterized at various batch injection rates and at two operating gas temperatures (280°F and 350°F). The mercury removal results for each sorbent at the two gas temperatures are shown in Figure 8. As shown,

both the A6 and CR325D performed slightly better than the baseline sorbent FGD. The AMS did not perform as well as the carbon-based sorbents. The impact of increasing the gas temperature from 280°F to 350°F decreased the mercury removal performance for all sorbents. The greatest difference was seen at the lower injection rates.

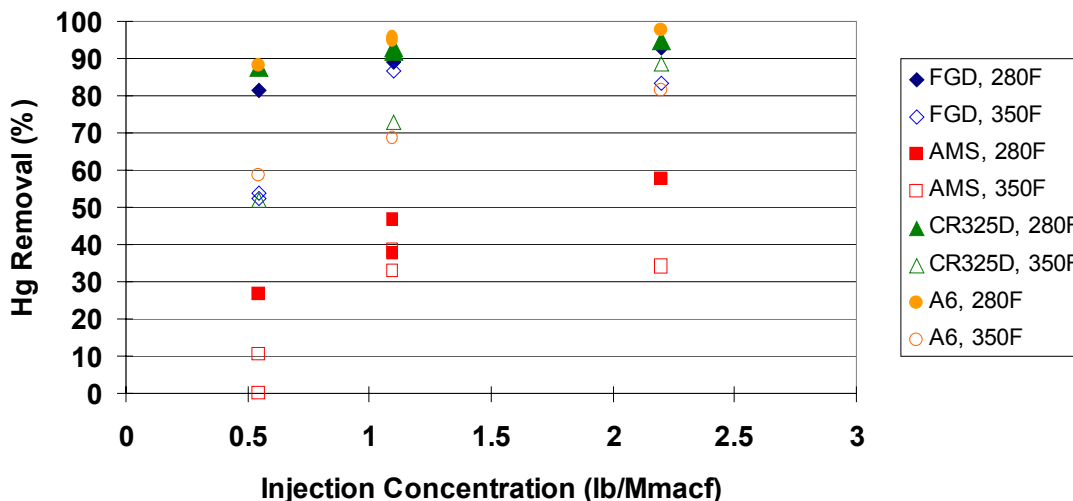


Figure 8. Mercury sorbent parametric evaluations on Unit 1 at P4.

4.2.6 P4 Unit 2 Parametric Results

Three mercury sorbents (AMS, A6, and CR325D) and the baseline sorbent FGD were evaluated on Unit 2 at various sorbent batch injection rates and two gas temperatures (300°F to 350°F). During the first evaluation period (December 5-9, 2003), the SCR catalyst was in place in Unit 2 but the ammonia flow was not activated. The second evaluation period occurred when the SCR was working as designed (January 14-22, 2004). As shown in Figure 9, the mercury removal decreased slightly for AMS and FGD when the SCR was online and the A6 and CR325D performed similarly under the two conditions. The open symbols represent the conditions when the SCR was offline.

Three additional sorbents (Thief, IAC, and CFA) were evaluated on Unit 2 at a gas temperature of 300°F and the results are shown in Figure 10. The performance at 0.5 lb/Mmacf ranged from 49% (Thief) to 66% (CFA) mercury removal.

Sorbent performance degraded slightly for the carbon-based sorbents with an increase in gas temperature from 300°F and 350°F. At a batch injection rate of 2.2 lb/Mmacf, the carbon-based sorbents performed similarly, with a mercury removal of 83% to 86%, as seen in Figure 11. The AMS mercury removal actually increased slightly at the higher injection rate and temperature.

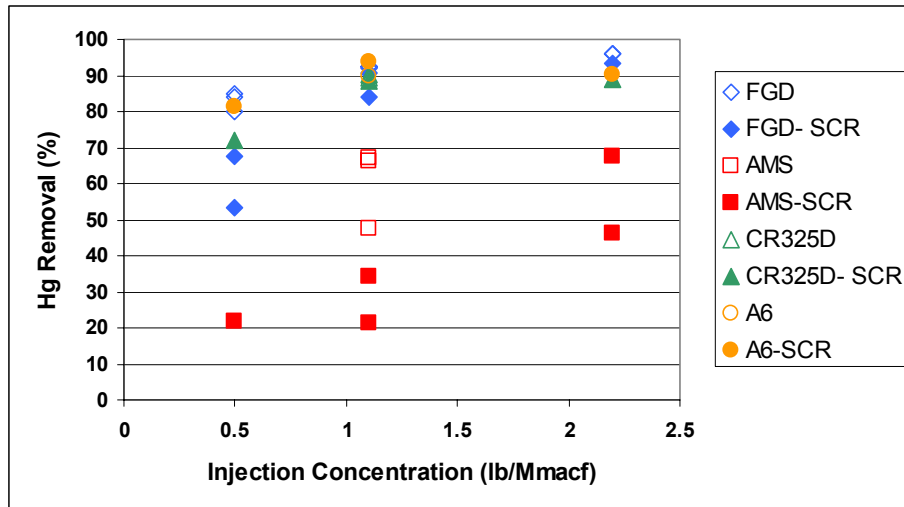


Figure 9. Parametric sorbent evaluations on P4's Unit 2 with and without SCR on line at a gas temperature of 300°F. Repeated data shown where available for individual sorbents.

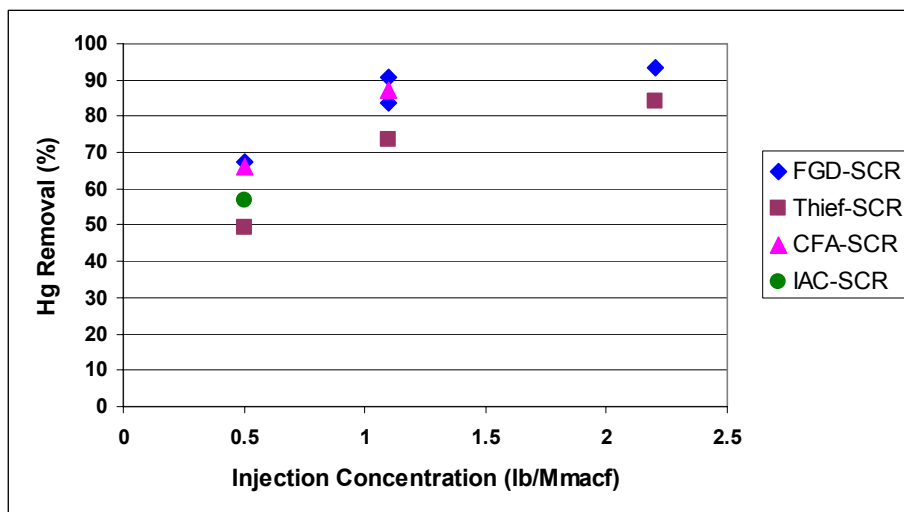


Figure 10. Parametric sorbent evaluations on P4's Unit 2 with SCR on line at a gas temperature of 300°F.

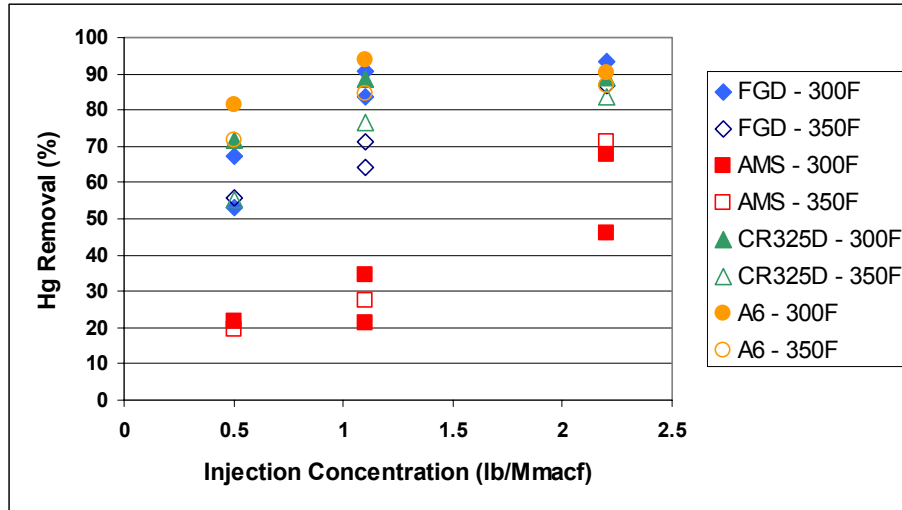


Figure 11. Parametric sorbent evaluations on P4's Unit 2 with SCR on line at two gas temperatures. Repeated data shown where available for individual sorbents.

4.3 By-product Results

During the long-term sorbent evaluations at Powerton and VAPP, by-product samples were collected in the baghouse hoppers for each sorbent evaluated. At Powerton, FGD, HOK, and CFA sorbents were evaluated long-term while at VAPP, FGD, A10, and CFA sorbents were evaluated. The term “by-product” is defined as fly ash and spent sorbent for this project. The results from the mercury analyses of the by-products, the simulated landfill tests, the leaching tests, and desorption tests are presented below.

4.3.1 Mercury Analyses on By-product Samples

Results from the mercury analysis of the Powerton and VAPP by-product samples are presented in Table 6 and Table 7, respectively.

Table 6. Powerton By-product Sample Mercury Concentration and LOI Data Summary.

Sample ID	Frontier Geosciences, $\mu\text{g/g}$	URS Corporation, $\mu\text{g/g}$	% LOI
Powerton Baseline Ash	-	1.34	3.31
FGD 6/22-6/23/02 - bag 1	5.53	5.48	5.78
FGD 6/22-6/23/02 - bag 2	-	5.99	6.33
HOK 6/28/02 - bag 1	8.73	11.70	7.15
HOK 6/28/02 - bag 2	-	15.26	11.98
CFA 6/30-7/1/02 - bag 1	9.3	10.13	15.24
CFA 6/30-7/1/02 - bag 2	-	8.55	20.61

* Note: bag 1 is a Teflon coated fiberglass bag and bag 2 is a 7.0-denier Torcon felt bag.

Table 7. VAPP By-product Sample Mercury Concentration and LOI Data Summary.

Sample ID	URS Corporation, $\mu\text{g/g Hg}$	% LOI
VAPP Baseline Ash	1.04	22.20
CFA 3/27/03 – bag 1	2.25	27.57
CFA 3/27/03 – bag 2	1.47	30.49
A10 4/3/03 – bag 1	1.23	25.85
A10 4/3/03 – bag 2	1.59	27.22
FGD 3/21/03 – bag 1	0.80	28.17
FGD 3/21/03 – bag 2	1.16	29.96

* Note: bag 1 is a 2.7-denier Ryton bag and bag 2 is a 7.0-denier Torcon felt bag.

As can be seen in Table 6, the two independent mercury concentration measurements for the Powerton by-product samples show relatively good agreement given typical variability from sample aliquot to sample aliquot.

The % LOI of the by-product samples from both sites increased with the addition of sorbent. The mercury concentration of the Powerton by-product samples increased substantially whereas the mercury concentration in the VAPP by-product samples did not show a major uptake of mercury for most samples.

The trend of increasing mercury concentration with increasing LOI, due to sorbent injection, was observed in the Powerton by-product samples containing the FGD sorbent and the HOK sorbent. However, this trend was not observed in the Powerton by-product sample containing the CFA sorbent. Although the CFA bag 1 sample did show higher

mercury concentrations than in the baseline ash, the bag 2 sample with the higher LOI showed less mercury content than the bag 1 sample at lower LOI (even after considering dilution by the sorbent added). The VAPP by-product samples showed considerably lower mercury concentrations than the Powerton by-products in spite of considerably higher LOI content which could be attributable to the lower in-duct vapor-phase mercury concentrations observed at VAPP. Although the long-term test samples all showed higher LOI content than the baseline sample, not all contained higher than baseline mercury concentrations.

4.3.2 Landfill Simulation Tests

Tables 8 and 9 summarize the results of the Powerton by-product sample landfill simulation tests, which were conducted with the by-product samples collected from baghouse 2 (Torcon). Tables 10 and 11 summarize the results of the VAPP by-product samples landfill simulation tests, which were conducted with the by-product samples collected from baghouse 1 (2.7-denier Ryton).

In each table, the initial ng of mercury available for desorption in the sample used is shown, followed by the mercury mass gain in the downstream Carulite mercury adsorption tubes after each measurement interval.

Table 8. Results of Powerton Room Temperature Landfill Simulation Tests.

Sample ID	Available Hg for desorption (ng)	Carulite Tube Hg Gain, ng of Hg						%Hg Loss
		2 weeks	8 weeks	14 weeks	18 weeks	24 weeks	Total Gain	
Powerton Baseline Ash	6,800	<11.3	<11.3	-	-	-	<22.6	<0.33
FGD Long Term 6/22-6/23/02 – bag 2	28,500	<11.3	<11.3	-	-	-	<22.6	<0.08
HOK 6/28/02 – bag 2	79,400	<11.3	<11.3	-	-	-	<22.6	<0.05
CFA 6/30-7/1/02 – bag 2	42,800	<11.3	<11.3	-	-	-	<22.6	<0.03

Table 9. Results of Powerton 140°F Landfill Simulation Tests.

Sample ID	Available Hg for desorption (ng)	Carulite Tube Hg Gain, ng of Hg						%Hg Loss
		2 weeks	8 weeks	14 weeks	18 weeks	24 weeks	Total Gain	
Powerton Baseline Ash	6,700	<11.3	<11.3	<11.3	<11.3	<11.3	<56.3	<1.01
FGD Long Term 6/22-6/23/02 – bag 2	29,950	<11.3	<11.3	<11.3	<11.3	<11.3	<56.3	<0.23
HOK 6/28/02 – bag 2	76,300	<11.3	<11.3	<11.3	<11.3	<11.3	<56.3	<0.09
CFA 6/30-7/1/02 – bag 2	42,750	<11.3	<11.3	<11.3	<11.3	<11.3	<56.3	<0.16

Table 10. Results of VAPP Room Temperature Landfill Simulation Tests.

Sample ID	Available Hg for desorption (ng)	Carulite Tube Hg Gain, ng of Hg					%Hg Loss
		2 weeks	8 weeks	14 weeks	18 weeks	Total Gain	
Baseline VAPP Ash 3/21/03	4,163	<13.2	<13.2	<13.2	<13.2	<53.0	<1.3
FGD 3/21/03 - bag 1	3,361	<13.2	<13.2	<13.2	<13.2	<53.0	<1.6
FGD 3/21/03 - bag 1 dup	3,621	<13.2	<13.2	<13.2	<13.2	<53.0	<1.5
CFA 3/27/03 - bag 1	9,667	<13.2	<13.2	<13.2	<13.2	<53.0	<0.5
A10 4/3/03 - bag 1	5,489	<13.2	<13.2	<13.2	<13.2	<53.0	<1.0

Table 11. Results of VAPP 140°F Landfill Simulation Tests.

Sample ID	Available Hg for desorption (ng)	Carulite Tube Hg Gain, ng of Hg					%Hg Loss
		2 weeks	8 weeks	14 weeks	18 weeks	Total Gain	
Baseline VAPP Ash 3/21/03	4,184	<13.2	<13.2	<13.2	<13.2	<53.0	<1.3
FGD 3/21/03 - bag 1	3,512	<13.2	<13.2	<13.2	<13.2	<53.0	<1.5
FGD 3/21/03 - bag 1 dup	3,606	<13.2	<13.2	<13.2	<13.2	<53.0	<1.5
CFA 3/27/03 - bag 1	9,898	<13.2	<13.2	<13.2	<13.2	<53.0	<0.5
A10 4/3/03 - bag 1	5,535	<13.2	<13.2	<13.2	<13.2	<53.0	<1.0

All of the individual results shown in the Tables 8-11 are “less than” values. These values are considered to be below measurable levels. The minimum measurable value was estimated to be three standard deviations about the mean mercury content of all of the method-blank Carulite tubes analyzed. For the Powerton by-product sample tests, the mean value of the method blanks was 5.2 ng and the standard deviation of the method blanks was 2.0 ng, so any mercury gain (or loss) of less than 11.3 ng was considered to be below measurable levels in these tests. The VAPP landfill simulations were run separately from the Powerton landfill simulations; therefore, they have a different set of method blanks and a different detection limit. For the VAPP by-product sample tests, the mean value of the method blanks was 3.1 ng and the standard deviation of the method blanks was 3.4 ng, so any mercury gain (or loss) of less than 13.2 ng was considered to be below measurable levels in these tests and treated as a zero value in the summations. No measurable amounts of mercury loss were observed for any of the by-product samples from Powerton or VAPP.

4.3.3 Leaching Tests

Results from the leaching tests performed on the Powerton and VAPP by-product samples are presented in Tables 12 and 13, respectively. The leachates produced from the various leaching procedures were analyzed for mercury, and those concentrations were compared to the Maximum Contaminant Level (MCL), which is related to Federal drinking water standards. The MCL criteria for mercury is 0.2 ppm, and none of the Powerton or VAPP samples were at the threshold of being considered hazardous by the MCL criteria. Most samples were below analytical detection limits for mercury.

Table 12. Leaching Results of the Powerton By-product Samples in SPLP Matrix and Water.

Sample ID	SPLP Matrix pH 2.5 mg/L Hg	SPLP Matrix pH 5.0 mg/L Hg	ASTM type II Water pH 7.0 mg/L Hg
Powerton Baseline Ash	<0.00006	<0.00006	<0.00006
FGD Long Term 6/22-6/23/02 – bag 1	<0.00006	<0.00006	0.00012
FGD Long Term 6/22-6/23/02 – bag 2	<0.00006	<0.00006	0.00017
HOK 6/28/02 – bag 1	<0.00006	<0.00006	<0.00006
HOK 6/28/02 – bag 2	<0.00006	<0.00006	<0.00006
CFA 6/30-7/1/02 – bag 1	<0.00006	<0.00006	<0.00006
CFA 6/30-7/1/02 – bag 2	<0.00006	<0.00006	<0.00006

Table 13. Leaching Results of the VAPP By-product Sample in SPLP Matrix, Water, 0.1M Na₂CO₃, and 0.1N H₂SO₄.

Sample ID	SPLP Matrix pH 4.2, mg/L Hg	ASTM Type II Water pH 7.0, mg/L Hg	0.1M Na₂CO₃ pH=11.4, mg/L Hg	0.1N H₂SO₄ pH=1.3, mg/L Hg
VAPP Baseline Ash 3/21/03	<0.00012	<0.00010	<0.00025	<0.00015
FGD 3/21/03 - bag 1	<0.00012	0.00015	<0.00025	<0.00015
FGD 3/21/03 - bag 2	<0.00012	<0.00010	<0.00025	<0.00015
CFA 3/27/03 - bag 1	<0.00012	<0.00010	<0.00025	0.00022
CFA 3/27/03 - bag 2	<0.00012	<0.00010	<0.00025	<0.00015
A10 4/3/03 - bag 1	<0.00012	<0.00010	<0.00025	0.00026
A10 4/3/03 - bag 2	<0.00012	0.00014	<0.00025	0.00032

4.3.4 Desorption Tests

Table 14 shows the desorption profile of each desorption test performed. The percent of mercury desorbed at each temperature is summarized. The percent desorbed represented in Table 14 was calculated by dividing the ng of mercury desorbed at each temperature by the total amount of available ng of Hg in the original sample.

Table 14. Powerton By-product Samples Desorption Profile.

Temp (F)	Base Ash		FGD		HOK		CFA	
	% desorb	Total % desorbed	% desorb	Total % desorbed	% desorb	Total % desorbed	% desorb	Total % desorbed
0-150	8.0	8.0	0.0	0.0	0.0	0.0	0.0	0.0
170	38.0	46.0						
200	0.0	46.0						
250	0.0	46.0	0.0	0.0	0.0	0.0	0.0	0.0 (0.0)
300	0.0	46.0						
350	1.8	47.8	13.7	13.7	6.7	6.7	0.0	0.0 (0.0)
400	3.9	51.7	18.7	32.4	1.4	8.1	7.0	7.0 (4.4)
450	5.8	57.5	47.9	80.3	14.3	22.4	60.7	67.7 (42.8)
500	3.5	61.0	8.7	89.0	14.2	36.6	80.2	147.9 (93.5)
550	6.3	67.3	5.1	94.1	0.4	37.0	5.3	153.2 (96.8)
600	0.5	67.8	3.5	97.6	2.4	39.4	2.7	155.9 (98.5)
650			1.4	99.0	0.7	40.1	2.3	158.2 (99.9)
700	1.1	68.9	0.6	99.6	0.0	40.1	0.0	158.2 (99.9)

The by-product samples containing sorbents lost mercury at higher temperatures than Powerton's baseline ash. The baseline ash sample lost 46% of its original mercury content by 200°F, while the samples containing sorbent did not lose any mercury up to

200°F. This suggests that sorbent-containing by-product mixtures will be less susceptible to mercury losses at high ambient temperatures. The by-product samples containing sorbents did desorb an appreciable amount of mercury as the temperature was increased. By-product samples containing FGD or CFA lost approximately 90% of the mercury during these evaluations by 500°F.

The only sample that saw all of the available mercury desorb was from the FGD by-product. The baseline and HOK by-product only desorbed 69% and 40%, respectively. The CFA by-product measured 158% of the original mercury content having been desorbed. It is not clear as to why the CFA sample saw greater than 100% desorption. This could have been due to a low bias in the measured mercury content of the sample tested, or problems in measuring and/or calculating mercury recoveries during this particular desorption test. Because the total amount of mercury recovered during the desorption test was greater than 100% of the original content, the second number was added in parentheses showing “normalized” mercury desorption percentages which were calculated assuming that 100% of the mercury in the original sample was recovered during the test.

VAPP by-product samples were not evaluated due to equipment and time constraints. Duplicate evaluations on the Powerton by-product samples would have been desirable to measure the repeatability of the desorption percentages, particularly for the CFA samples. Sand blank tests were run, and all saw no measurable mercury desorption.

These results suggest that the FGD and CFA sorbents could possibly be regenerated, since both showed high percentage mercury desorption. The HOK sorbent looked less likely to be regenerable.

5.0 Economic Analyses

Dr. Massoud Rostam-Abadi with the Illinois State Geological Survey performed an engineering economic analysis to estimate the production costs of the most promising novel sorbents. An independent contractor reviewed and critically assessed the cost estimates.

There are various ways to examine sorbent costs. A bottom-up buildup of the cost of production for a given quantity, followed by adding overhead/administrative costs and an estimated profit margin, is one approach. This type of buildup is extremely sensitive to the assumptions made both technically and commercially. For the novel sorbents evaluated here, primarily CS80 and CFA, critical assumptions include the source of material supply, site location, and quantity of carbon product demanded. In the pricing provided herein, these assumptions are described in some more detail, and their relevance to the market discussed.

Another important parameter when examining projected costs is the competing prices and commercial offerings available in the marketplace. This puts the sorbent's price into context. This of course is difficult without having insight into competing sorbent

manufacturers' businesses. Projected future prices of the competition are speculative. An important point to note relative to these prices is that the current market is one in which supply capacity exceeds demand. The beginning of use of carbon-based sorbents for mercury control on coal-fired power plants will change this situation. Buyers will find themselves in a weak position, with demand outstripping supply capacity. This will most likely drive sorbent prices up until supply catches up.

Three sorbents are priced in detail in this exercise. One is a biomass-based sorbent, the second is an oil-based sorbent, and the third is a lignite-based activated carbon. Each price provided is FOB point of manufacture, and assumes a small business centered around production, with minimal staffing. This is a niche application for carbon-based sorbents, since it does not address a larger market that will demand large supply quantities or backing by a large corporation that can absolutely guarantee supply reliability and quality control.

Items included in the pricing are:

- Basic production cost, including raw materials and the variable costs of manufacture (labor, power, consumables, etc);
- Marketing costs are minimal because of the captive market assumed in these scenarios; when they are included they are 1.5%-4.5% of basic production cost;
- General & Administrative cost at about 5% of basic production cost;
- Capital recovery, at an interest rate of 6%;
- Reasonable profit.

What is not included is a large corporation that supports marketing, research and development, and ongoing expansion efforts.

Lignite Activated Carbon (LAC)

For comparison purposes, pricing for LAC was calculated using the same methodology as for the novel sorbents. The LAC pricing assumes that 4.5 power plants of 1,000 MW rating are supplied (quantity is based on 5 lb/Mmacf carbon). Ten-year financing is used, and the largest practical kiln sizes are employed. At a mine mouth location, 12,500 ton/yr of LAC can be supplied for under \$5,000,000, or less than \$0.20/lb.

This LAC approach could supply a handful of power plants located adjacent to mines, and still may be competitive if shipped within a region. The pricing is significantly lower than current commercial pricing. This is attributable to assuming a small, captive market, appropriate location of the end-user, and simplified processing to obtain the minimum surface area appropriate for the user application of dry sorbent injection for mercury control. In addition, current coal pricing is assumed. This raw material cost is subject to the variability of the coal market.

CS80

The CS80 pricing is calculated for two supply scenarios. The first assumes that one power plant of 1,000 MW rating is supplied (quantity is based on 5 lb/Mmacf carbon) via an on-site, dedicated processing facility. Sixteen-year financing is used. For this example, 2,800 ton/yr of CS80 could be supplied for about 10% less per pound than LAC.

The second scenario for CS80 is for a larger supply; 10.7 power plants of 1,000 MW rated capacity. In this case, an existing CS80 plant's facilities are expanded to generate the new supply. With the simplified permitting process and economy of scale, this quantity can be supplied at about 30% less per pound than LAC.

CFA

The CFA pricing is for 7.9 power plants of 1,000 MW rating. Ten-year financing is used. It is assumed that 22,000 ton/yr of CFA could be supplied for under \$11,000,000, or less than \$0.25 per pound.

The biomass material required for CFA manufacture has limited supply, and may not be widely expandable. Further optimization of the processing of this material may reduce the variable costs.

Table 15 shows current commercial pricing and compares it with pricing for the novel sorbents described here.

Table 15. Sorbent Pricing Comparison.

Sorbent Description	Quantity	Price Range, \$/lb
Commercial Powdered Activated Carbons today	Supersack size or greater (≥900 lb)	0.30-0.45
LAC: small quantity, captive supply	12,500 ton/yr	<0.20
CS80	2,800 ton/yr	<0.18
	30,000 ton/yr	<0.15
CFA	22,000 ton/yr	<0.25

The costs in Table 15 show that mercury control sorbent costs are likely to come down in a competitive marketplace. Although larger companies with more marketing infrastructure, reliability, and negotiating power will supply a large share of the sorbent market, smaller enterprises certainly have the opportunity to provide a lower price to their customers under the right set of circumstances.

6.0 Conclusions

Numerous novel sorbents (5 at Powerton, 17 at VAPP, and 19 at P4) were evaluated for use in mercury control technologies involving sorbent injection. The baseline sorbent was FGD and was evaluated at the three sites. The performance screening results of FGD and five other sorbents evaluated at two or more sites are presented in Figure 12. The performance of the sorbents and FGD did not vary much between the three sites (within 10% with comparable injection rates). The sorbent screening parameters for each site were presented earlier.

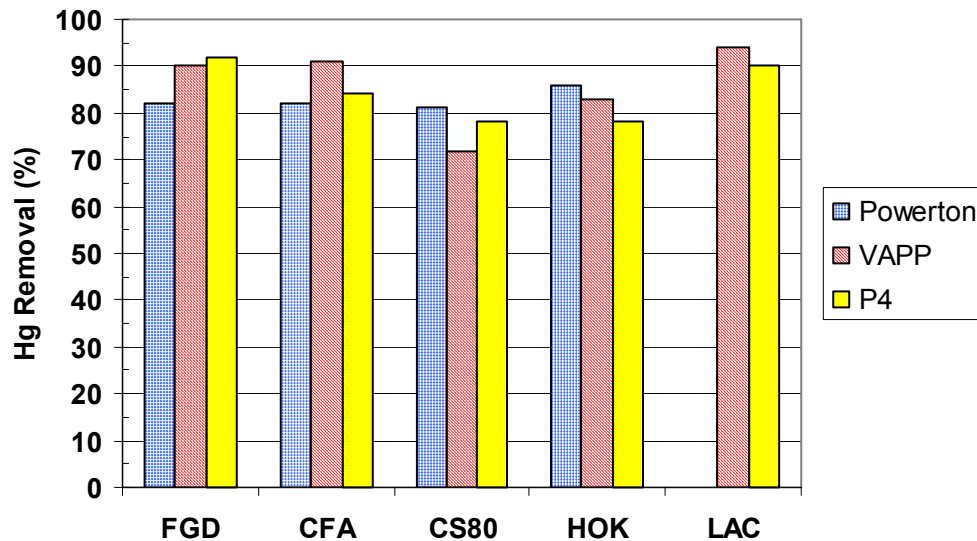


Figure 12. Sorbent comparison for mercury removal at the three test sites.

The best performing sorbents were carbon-based as demonstrated at the three field locations. Performance of the carbon-based sorbents varied and the mercury removal could not be correlated to the amount of modification (i.e. activation or treatment) performed on the base sorbent. Specialty carbons, such as IAC, were included in the program since they have demonstrated enhanced performance at unique plant sites. Their performance (lower injection concentrations required in some cases) may offset the higher up front cost (\$7/lb), which may provide an economic advantage with specific coals and plant operations. Please note the results for the IAC screening were at injection concentrations much less than that of the other sorbents during screening. For the IAC, the injection concentrations were 0.6, 1.7, and 0.5 lb/Mmacf for Powerton, VAPP, and P4, respectively.

Non carbon-based sorbents (i.e. AMS and Thief) although not as effective as the carbon-based sorbents tested, may have an economic benefit where by-product resale/utilization

is an economic consideration. This program did not attempt to validate claims by the sorbent suppliers as to their impact on fly ash reuse. Performance of the sorbents grouped in the “other” category varied depending on the base material (flyash, zeolite, other). The zeolite-based sorbents performed better than the fly ash-based sorbents during sorbent screening at VAPP and P4. Both the Thief and AMS sorbents removed greater than 60% of the incoming mercury in the TOXECON configuration at P4.

Temperature of the flue gas did not significantly affect sorbent performance in the COHPAC or residence chamber configurations at Powerton. At VAPP, mercury removal increased slightly at the higher temperature (315°F to 350°F) for all three sorbents evaluated in the COHPAC configuration but not in the residence chamber configuration. In addition, sorbent performance increased with increased residence time and injection concentration at both VAPP and Powerton. At P4, the impact of increasing the gas temperature from 280°F to 350°F decreased the mercury removal performance for all sorbents evaluated. The greatest difference was seen at the lower injection rates. Other plant characteristics may influence sorbent performance and the effect of temperature had on sorbent performance may not be universal to all plants burning similar coals as demonstrated in this program.

Re-injection of sorbent/by-product was evaluated at Powerton using the HOK sorbent and demonstrated 53% mercury removal compared to 83% mercury removal with fresh sorbent. Depending on the plant conditions, costs, and mercury removal required, this could be an option for reducing mercury sorbent injection control costs.

Results of the by-product analysis demonstrated that no mercury was released during the air stability or leaching evaluations.

Sorbent economics will be driven by the supply and demand. If there are viable resources located within close proximity of coal-fired utilities, then lower cost options may be available on a case by case basis. Price of the sorbent will also depend on the required mercury reduction needed by the individual utilities. With the information presented on the two coal types, there are a wide range of sorbents that could be made available to satisfy utilities that require 30% to 70% mercury removal when using a similar particulate control scenario. Other plant issues also need to be addressed when considering sorbent injection with the impact on the sale of by-products being at the top of the list. A sorbent’s overall economic impact needs to be taken into account when considering the control technology and cost of mercury control. Again, the overall cost of the sorbents evaluated during this program were not independently verified. Although larger companies with more marketing infrastructure, reliability, and negotiating power will supply a large share of the sorbent market, smaller enterprises certainly have the opportunity to provide a lower price to their customers under the right set of circumstances.

Appendix A. Description of Mercury Monitors and Sampling Procedures

A.1 Description of Mercury Monitor

A semi-continuous mercury emissions monitor (S-CEM) was used during this program to provide near real-time feedback during baseline, screening, and long-term testing. Continuous measurement of mercury at the inlet and outlet of the particulate collector is considered a critical component of a field mercury control program where mercury levels fluctuate with boiler operation (temperature, load, etc.) and decisions must be made concerning parameters such as sorbent feed rate and cooling. The analyzer used for these tests consisted of a cold vapor atomic absorption spectrometer (CVAAS) coupled with a gold amalgamation system (Au-CVAAS). The system is calibrated using vapor-phase elemental mercury. A sketch of the system is shown in Figure A-1. The S-CEM was configured to automatically switch from measuring total vapor-phase mercury to vapor-phase elemental mercury during these tests. A photograph of the S-CEM installed at a field site is shown in Figure A-2.

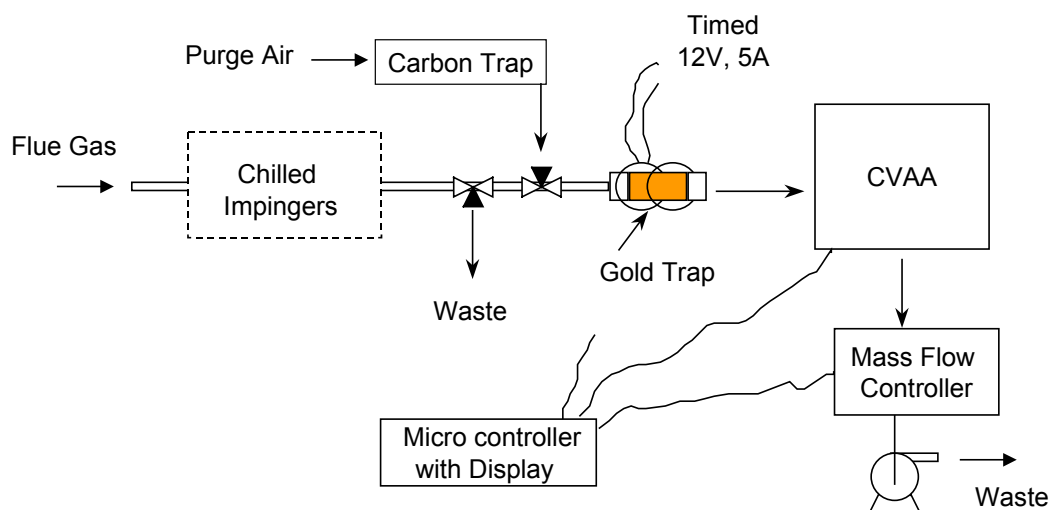


Figure A-1. Sketch of mercury measurement system.



Figure A-2. Photograph of Apogee mercury S-CEM installed at a field site.

Although it is very difficult to transport non-elemental mercury in sampling lines, elemental mercury can be transported without significant problems. Since the Au-CVAAS measures mercury by using the distinct lines of the UV absorption characteristic of Hg^0 , the non-elemental fraction is either converted to elemental mercury (for total mercury measurement) or removed (for measurement of the elemental fraction) near the sample extraction point. This minimizes any losses due to the sampling system.

For total vapor-phase mercury measurements, all non-elemental vapor-phase mercury in the flue gas must be converted to elemental mercury. A reduction solution of stannous chloride in hydrochloric acid is used to convert Hg^{2+} to Hg^0 . The solution is mixed as prescribed in the draft Ontario Hydro Method for Manual Mercury Measurements. To measure speciated mercury, an impinger of potassium chloride (KCl) solution mixed as prescribed by the draft Ontario Hydro Method replaces the stannous chloride solution to capture oxidized mercury. The impinger solutions are continuously refreshed to assure continuous exposure of the gas to active chemicals.

A.2 Sampling Procedures and QA/QC

During testing, the analyzer sampling time is set to collect nominally 20 ng of mercury per sampling cycle. The noise level of the analyzer operating at a field site is approximately 1 ng, thus collecting 20 ng provides a signal-to-noise ratio of 20.

The mercury monitor is calibrated following installation at the field site for mercury, sample flow rate, and oxygen concentration. The calibration of both the Au-CVAA analyzer, which measures the mass of mercury desorbed, and the mass flow controller in the monitor, which measures the total sample volume through the analyzer, is checked daily during testing. The analyzer is calibrated by introducing a spike of vapor-phase elemental mercury into the analyzer upstream of the gold wire. The mercury vapor for the spike is drawn from the air space in a vial containing liquid elemental mercury. The mercury spike concentration is calculated from the vapor pressure of mercury and the temperature of the vial. The vial temperature is measured with a precision thermistor. Connecting the operating controller in series with a calibrated mass flow controller checks the calibration of the mass flow controller within the S-CEM.

Documentation of analyzer calibration is recorded on calibration data sheets and any system maintenance is recorded in the project notebook. A calibration file for additional equipment, which contains manufacturers' certification of calibration, is maintained by Apogee Scientific.

Data verification of computer calculations is conducted manually on a periodic basis. Any data collected during periods of suspected operational inconsistencies is rejected as questionable data.

A.3 Bench Scale Fixed Bed Adsorption Test Device

Mercury adsorption tests are conducted by measuring the mercury capacity for sorbents in the presence of mercury-laden flue gas. The test apparatus is illustrated in Figure A-3. Sorbents are mixed in a sand diluent prior to being packed in a temperature-controlled, adsorption column (1.27 cm ID). A ratio of 20 mg sorbent to 10 g of sand is generally used for carbon-based sorbents and zeolites, and 200 mg sorbent to 10 g of sand was used for fly ashes. These mass-loadings are chosen to achieve reasonable mercury breakthrough times with the respective sorbents. Prior to flue gas exposure, the sorbent fixed-bed is heated to the desired temperature for periods up to one hour. During this time, the flue gas is by-passed directly to the analytical system to determine the "inlet" mercury concentration. Adsorption tests were initiated by flowing flue gas downward through the fixed-bed column at a flow rate near 1 L/min. Mercury measurements are made with a mercury S-CEM.

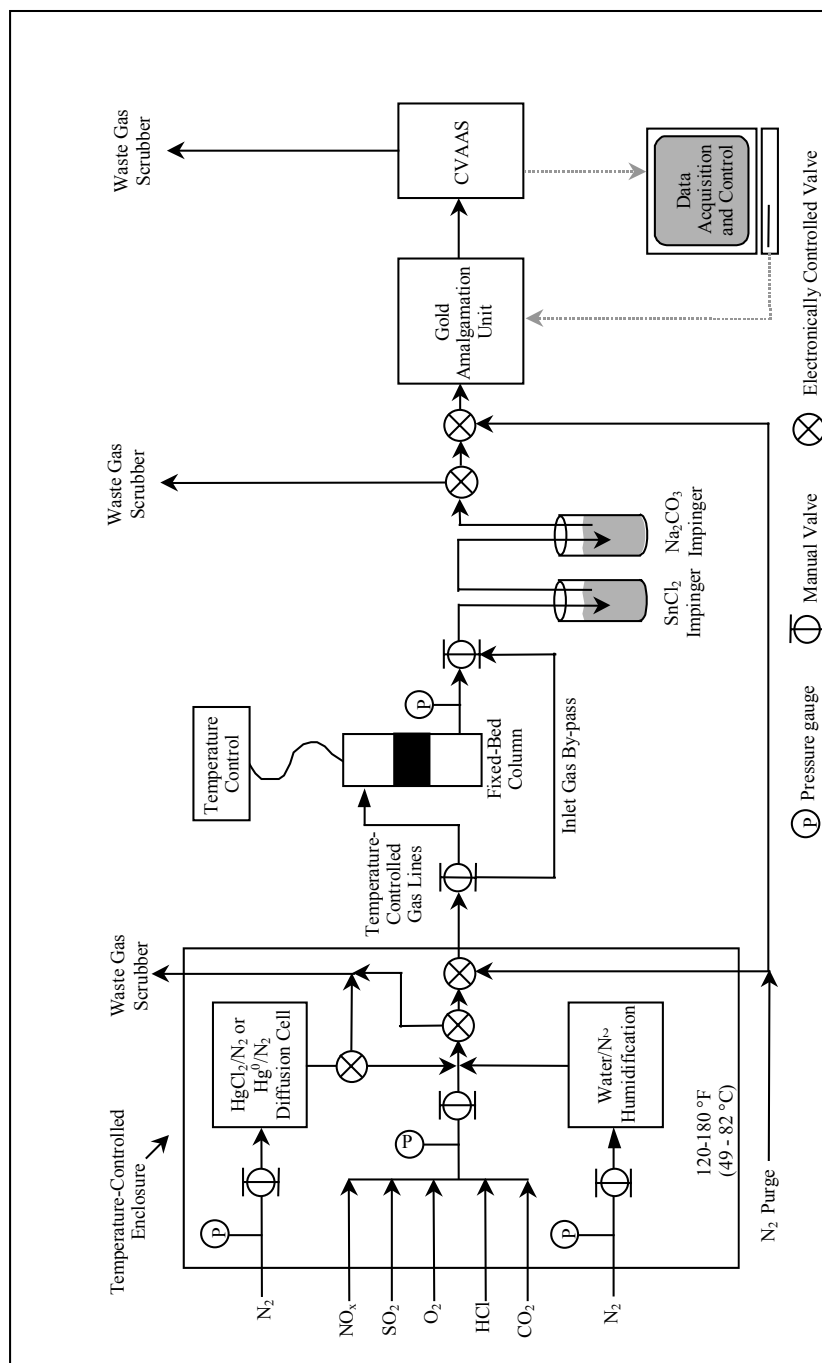


Figure A-3. Bench Scale Fixed Bed Adsorption Test Device.

The amount of mercury exiting the sorbent column is measured on a semi-continuous basis. Gas is passed through the column until 100% of the inlet mercury is detected at the outlet (100% breakthrough). The 100% breakthrough (equilibrium) capacity of the sorbent ($\mu\text{g Hg/g sorbent}$) is determined by summing the total mercury adsorbed until the time when the outlet mercury concentration is first equal to the inlet concentration. A more detailed description of the adsorption test apparatus can be found elsewhere (8).

Appendix B. By-Product Equipment and Procedures

B.1 Procedures

The stability of adsorbed mercury is important to study if the spent fly ash by-products are landfilled or reused. The following studies were intended to investigate whether the adsorbed mercury will be released back to the environment via volatilization or leaching into groundwater. According to the EPA Mercury Report to Congress, some work has been done with ash samples from municipal waste combustors (MWCs) while using carbon injection for mercury removal. The data suggest revolatilization of mercury is minimal.

The fly ash samples generated during this project underwent an air stability test for six months and an aqueous stability test by the EPA 1312 leaching procedure. The purpose of this testing was to simulate conditions the ash by-product may encounter in a landfill environment. The test procedures are described below in more detail.

B.1.1 Air Stability Testing Procedure and Conditions

The fly ash/sorbent by-product samples resulting from sorbent injection could be disposed of in a landfill. These by-products will contain an increased amount of mercury relative to the baseline fly ash that could potentially release back into the environment via air or water. To evaluate the potential of mercury volatilization, the by-products from the sorbent injection tests underwent a landfill simulation test. Figure B-1 is an illustration of the landfill simulation setup. These tests were conducted by placing a known amount of sample in a closed glass container and exposing that sample to a high flow rate of air for periods ranging from 8 to 24 weeks. The air entered the vessel, contacted the solid, exited the vessel, and passed through a Carulite sorbent tube. Any desorbed mercury exited the glass container with the effluent and passed through the Carulite tube. The air exiting the tube then proceeded into a water bubbler used for flow verification.

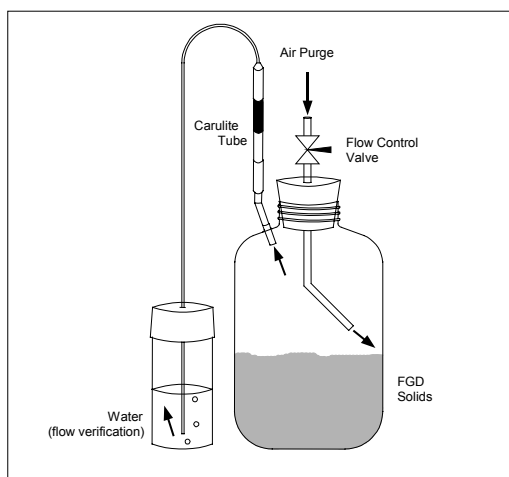


Figure B- 1. Schematic of the Landfill Simulation Test Set Up.

Carulite is a commercial sorbent, which is composed of greater than 90% manganese dioxide and is accepted for use in the NIOSH 6009 sampling method to measure mercury in ambient air. All Carulite tubes were packed on site in acid cleaned glass tubes with $0.5000\text{g} \pm 0.0010\text{g}$ of solid. The Carulite tubes were changed periodically throughout the six-month test period and analyzed for mercury capture. Table B-1 summarizes the nominal time periods over which the Carulite tubes were changed once the test started. Appropriate blank, spike, and duplicates tests were also run.

Table B-1. Landfill Simulation Carulite Change Schedule (± 1 week).

Test Description	Change 1	Change 2	Change 3	Change 4	Change 5
Powerton Room Temp	2 weeks	6 weeks	8 weeks (stop test)	-	-
Powerton 140°F	2 weeks	6 weeks	12 weeks	18 weeks	24 weeks (stop test)
VAPP Room Temp	2 weeks	6 weeks	12 weeks	18 weeks (stop test)	-
VAPP 140°F	2 weeks	6 weeks	12 weeks	18 weeks (stop test)	-

At the end of the landfill simulation tests, the approximate percent mercury released was calculated by adding the nanograms (ng) of mercury captured on each Carulite tube and dividing this sum by the total ng of mercury in the original sample aliquot available for desorption. Landfill tests were conducted at ambient temperature ($\approx 75^\circ\text{F}$) and at 140°F . The higher temperature was meant to represent the highest temperature the byproducts might encounter at high ambient temperature and direct sunlight heating.

The 140°F tests were conducted using the schematic illustrated in Figure B-1 except the glass bottles were placed in an oven that was set to maintain that elevated temperature. Figure B-2 is a photograph of the room temperature landfill simulation test set-up, and Figure B-3 is a photograph of the 140°F landfill simulation test set-up.

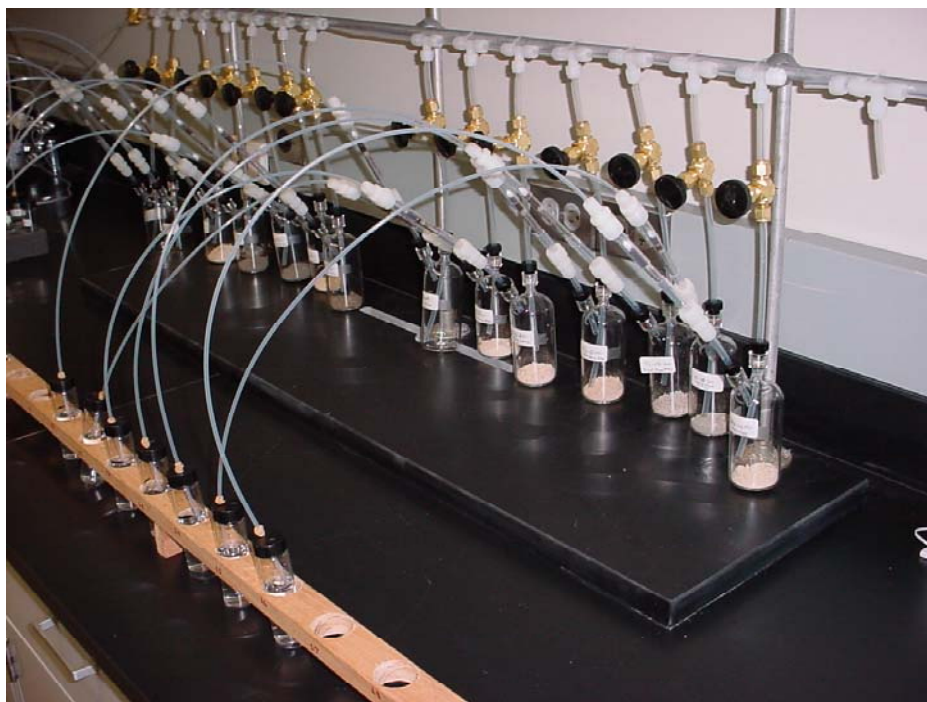


Figure B-2. Photograph of the Room Temperature Landfill Test Set Up.

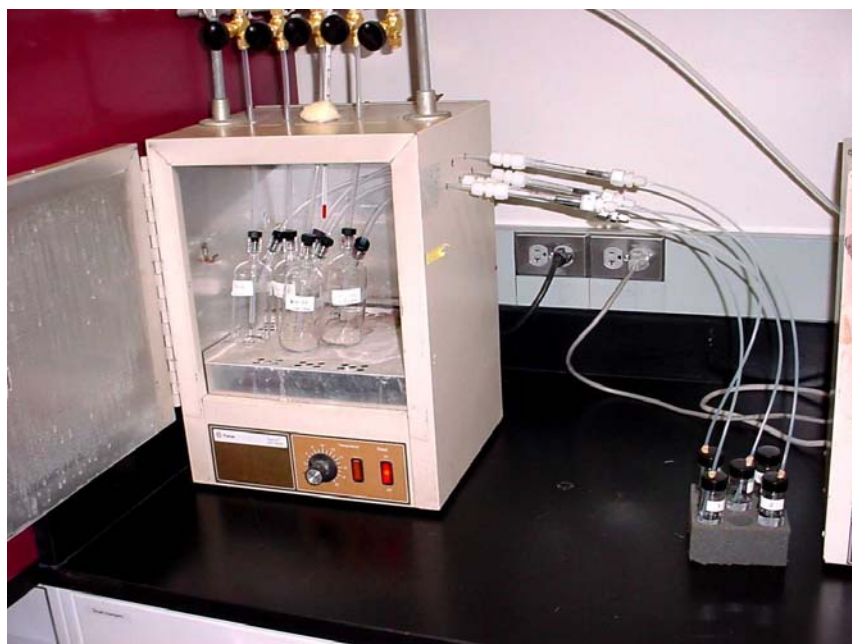


Figure B-3. Photograph of the 140°F Landfill Test Set Up.

The landfill simulations were run using a high flow rate of air, which was intended to represent windy ambient conditions. The rate was chosen to be approximately 50 mL/min. All flow rates were measured with a digital flow meter periodically throughout the tests, and before and after each Carulite change. The flow rate ranged from 45 to 55 mL/min throughout the Powerton by-product samples room temperature landfill simulation 8-week test period, and ranged from 44 to 54 mL/min throughout the Powerton by-product sample 140°F landfill simulation 24-week test period. The flow rate ranged from 46 to 55 mL/min throughout the VAPP by-product sample room temperature landfill simulation 18-week test period, and ranged from 50 to 55 mL/min throughout the VAPP by-product sample 140°F landfill simulation 18-week test period.

The ambient temperature in the laboratory was monitored with a digital thermometer that has the capability of recording the maximum and minimum temperature reached over a period of time. These temperatures were recorded periodically throughout the landfill simulation test periods. The average observed temperature for the Powerton by-product sample room temperature simulation tests was 72.9°F, while the average observed temperature for the VAPP by-product sample room temperature simulation tests was 69.1°F. The average temperature of the Powerton by-product sample 140°F simulation test was 139.8°F, while the average temperature of the VAPP by-product sample 140°F simulation test was 141.6°F.

Before the landfill simulation tests were started, a portion of each sample was analyzed for mercury. By-product samples containing sorbent were analyzed for mercury using ASTM method D3684 that involved the use of an oxygen Parr Bomb. The baseline ashes were analyzed for mercury by a conventional hydrofluoric acid digestion. Furthermore, due to the limited amount of the Powerton samples, the room temperature landfill simulation tests were run for an 8-week period rather than a 24-week period. These samples were recovered and used for the testing described in the next section.

B.1.2 Mercury Desorption Tests

Desorption tests were performed on the Powerton by-product samples. These tests used cold vapor atomic adsorption (CVAA) to measure the amount of mercury desorbed from the sample as a function of temperature. One gram (g) of solid was combined with 9g of acid cleaned sand and placed in a clean glass column. Next, approximately 750mL/min of air was passed through the column while the temperature was raised incrementally until most of the mercury was desorbed. The desorbed mercury was captured on a gold column, and then thermally desorbed and measured by CVAA. The purpose of this test was to determine at what temperatures the mercury would desorb from the by-product sample. This information could give insight into how strongly the mercury is bound to the sorbent. This may indicate whether the by-product sample could be regenerated for reuse as a mercury sorbent. The tests were started at room temperature and raised quickly to 140°F. Next, the temperature was raised in the following increments: 250°F, 350°F, 400°F, 450°F, 500°F, 550°F, 600°F, and 700°F. Each temperature was held until mercury desorption was no longer observed. Blank data were also acquired.

B.1.3 Leaching Test Procedure and Conditions

All samples were tested using EPA method 1312-Synthetic Precipitation Leaching Procedure (SPLP). As stated by the method, a 1:20 solid to liquid ratio was the criteria used for each sample set. EPA method 1312 was selected under the theory it would simulate the conditions relevant to the type of landfill an ash byproduct would be disposed in. This method simulates “acid rain” using sulfuric acid and nitric acid. The Powerton by-product samples were tested using the SPLP matrix at pH’s of 2.5 and 5.0, and at a pH of 7.0 using ASTM type II water. The VAPP by-product samples were tested using the SPLP matrix at a pH of 4.2, ASTM type II water (pH=7), 0.1M Na₂CO₃ (pH = 11.42), and 0.1N H₂SO₄ (pH=1.30). The sorbent/fluid mixtures were rotated at 28 to 32 rpm in a rotary extractor device for 16 to 20 hours at room temperature. Next, the samples were filtered using acid cleaned glassware and glass fiber filters, and the leachates were analyzed for mercury concentrations using EPA method 7470. The appropriate blanks, duplicates, and spike samples were also tested. Each result was compared to untreated sorbent material.

Appendix C. Sorbent Information

Sorbent Vendor	Sorbent Name	Site Evaluated
Norit Americas Inc.	FGD	Powerton, VAPP, and P4
	2002-8680 and 2002-8567	VAPP
Illinois State Geological Survey	CFA	Powerton, VAPP, and P4
	CS80	Powerton, VAPP, and P4
	LAC	VAPP and P4
EnviroTire Technologies, Ltd.	TDAC	Powerton, VAPP, and P4
Donau Carbon	HOK	Powerton, VAPP, and P4
Separation Technologies, Inc.	STI-020513-B, 020930-C, A	VAPP
	STI-B	Powerton
Barneby Sutcliffe Corp.	IAC and IAC 020430-B	Powerton, VAPP, and P4
ARKAY Technologies, Inc.	S-1 and E-1-S	VAPP
Physical Sciences Inc.	PSI-C	VAPP
Sorbent Technologies, Inc.	A10 and G	VAPP
	A6 and A5	P4
CarboChem Inc.	MC-40, MG-20	P4
Amended Silicates LLC	AMS	P4
Penn State University	FA1	P4
Carbon Resources, LLC	CR325A and CR325D	P4
United Manufacturing International	UMI-FG9B	P4
Superior Adsorbents, Inc.	Sample 1 and 2	P4
DOE/NETL	Thief	P4
Praxair, Inc.	PRA58	P4

Appendix D. Laboratory Sorbent Fixed-Bed Evaluations

Table D-1. Results from Laboratory Fixed-Bed Mercury Adsorption Capacity Tests on Simulated Low Sulfur Eastern Bituminous Flue Gas.

Vendor	Sample Name	Temp. (°F)	HgCl ₂ Equil. Ads. Cap. at 50 µg HgCl ₂ / Nm ³ (µg/g)	Hg ⁰ Equil. Ads. Cap. at 50 µg Hg ⁰ / Nm ³ (µg/g)
Advanced Fuel Research	AFR-g	275	1797	
Advanced Fuel Research	AFR-2	275	961	
Arkay	E-5-CN-02	275	115	
Arkay	E-4-A-02	275	1	
Arkay	E-3-CC-02	275	93	
Carbochem	FGC	275	2303	
Carbochem	IGC	275	1625	
Carbochem	PC-50	275	261	
Donau	GAL - ISGS	275	1150	
Donau	HOK	275	1750	
Dynamic Catalysts and Adsorbants	Dynasorb-200	275	0	
Dynamic Catalysts and Adsorbants	Dynasorb-E Cat	275	16	
Norit	FGD	275	1494	618
Norit	FGD Fines	275	3475	1687
Norit	Hydro Darco	275	2131	
Norit	FGL	275	1901	916
Norit	FGD/HCl	275	1239	-
Norit	FGD/Lime	275	1620	784
Physical Sciences Inc.	PSI-A	275	1672	
Physical Sciences Inc.	PSI-B	275	4172	
Physical Sciences Inc.	PSI-C	275	4047	
Physical Sciences Inc.	PSI-D	275	2468	
Superior Adsorbants, Inc.	SAI-A	275	520	
Superior Adsorbants, Inc.	SAI-B	275	614	
Sorbent Technologies, Inc.	Sorbtech A	275	2007	
Sorbent Technologies, Inc.	Sorbtech B	275	2417	
Sorbent Technologies, Inc.	Sorbtech C	275	368	
Sorbent Technologies, Inc.	Sorbtech D	275	288	
Sorbent Technologies, Inc.	Sorbtech E	275	311	
Sorbent Technologies, Inc.	Sorbtech F	275	279	
Sorbent Technologies, Inc.	Sorbtech I	275	399	
Sorbent Technologies, Inc.	Sorbtech J	275	615	
Sorbent Technologies, Inc.	Sorbtech K	275	257	
Sorbent Technologies, Inc.	Sorbtech L	275	1719	
ISGS	LAC-0101	275	2196	555
ISGS	Pilot-5	325	684	185
ISGS	CFA-6	275	1160	1288
ISGS	TDAC-00	275	922	444
ISGS	IPAC-5	325	238	94
ISGS	PDAC-Pilot	325	347	1129
American Absorbents Natural Products	AANP Zeolite-200	325	-	30
	NaA Zeolite	325	0	0
Comercial Zeolite modified by ISGS	NaA-S400	325	2825	25
ISGS	Soot 60	275	308	-
ISGS	Soot 80	275	990	-

Appendix D (cont.)

Table D-2. Results from Laboratory Fixed-Bed Mercury Adsorption Capacity Tests on Simulated PRB Flue Gas.

Vendor	Sample Name	Temp. (°F)	Hg ⁰ Equil. Ads. Cap. at 50 µg HgCl ₂ / Nm ³ (µg/g)	Hg ⁰ Equil. Ads. Cap. at 50 µg Hg ⁰ / Nm ³ (µg/g)
Norit	FGD	275	903	
Advanced Fuel Research	AFR-g	275	314	
Arkay	W-4-A-02	275	3	
Arkay	W-3-CC-02	275	5	
Superior Adsorbants, Inc.	SAI-A	275	298	
Superior Adsorbants, Inc.	SAI-B	275	365	
Sorbent Technologies, Inc.	Sorbtech A	275	2148	
Sorbent Technologies, Inc.	Sorbtech B	275	2460	
Sorbent Technologies, Inc.	Sorbtech C	275	232	
Sorbent Technologies, Inc.	Sorbtech D	275	208	
Sorbent Technologies, Inc.	Sorbtech E	275	164	
Sorbent Technologies, Inc.	Sorbtech L	275	2453	
Donau	GAL-ISGS	275	716	
Physical Sciences Inc	PSI-C	275	61	
Norit	FGD	325		450
ISGS	LAC-0101	325		670
ISGS	Pilot-5	325		412
ISGS	CFA-6	325		847
ISGS	TDAC-00	325		227
ISGS	IPAC-5	325		84
ISGS	PDAC-Pilot	325		201
American Absorbents Natural Products	AANP Zeolite-200	325		37
	NaA Zeolite	325		9
	NaA-S400	325		5
ISGS	Soot 60	275		264
ISGS	Soot 80	275		1313

References

1. J.H. Pavlish, et al., "Status review of mercury control options for coal-fired power plants", *Fuel Processing Technology*, 82, 89-165, 2003.
2. T.R. Carey, O.W. Hargrove, C.F. Richardson, "Factors affecting mercury control in utility flue gas using sorbent injection", Proceedings of the Air and Waste Management Association 90th Annual Meeting, Toronto, Ontario, Canada, June 8-13, 1997.
3. R. Chang, G. Offen, *Power Engineering*, November, 51-57, 1995.
4. "Development and Evaluation of Low-Cost Sorbents for Removal of Mercury Emissions from Coal Combustion Flue Gas," EPRI Report TR-110532, EPRI, Palo Alto, CA, 1998.
5. C.R. Carey, O.W. Hargrove, C.F. Richardson, R. Chang, F.B. Meserole, *J. Air & Waste Management Association*, 48, December, 1166-1174, 1998.
6. A. Attar, *Fuel*, 57, 201-212, 1978.
7. Data from EPA Information Collection Request for Mercury at Electric Utility Steam Generating Units, 1999.
8. "Laboratory Investigations and Model Development of Flue Gas Mercury Adsorption Using Solid Sorbents," EPRI Report TR-110533, EPRI, Palo Alto, CA, 1998.
9. R.D. Vidic, S. Kwon, D.P. Siler, "Impregnated activated carbons for elemental mercury adsorption", Proceedings of the 17th Annual Pittsburgh Coal Conference, , Paper 19a-3, Pittsburgh, PA, September 11-14, 2000.
10. W. Liu, R.D. Vidic, T.D. Brown, "Optimization of sulfur impregnation protocol for fixed-bed application of activated carbon-based sorbents for gas-phase mercury removal", *Environ. Sci. Technol.*, 32, 531-538, 1998.